TEXTILE RESEARCH JOURNAL

VOLUME XXIII January, 1953 *NUMBER 1*

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE

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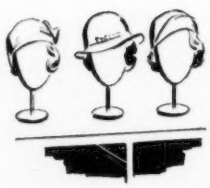

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the editorial office, 10 East 40th Street, New York 16, N. Y.

Subscription rates:
$15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $1.50 each.

Entered as second-class matter, April 27, 1945, at the post office at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

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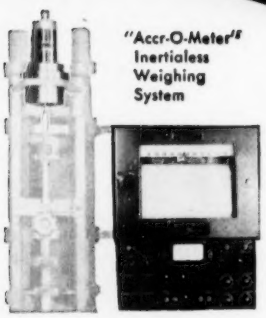

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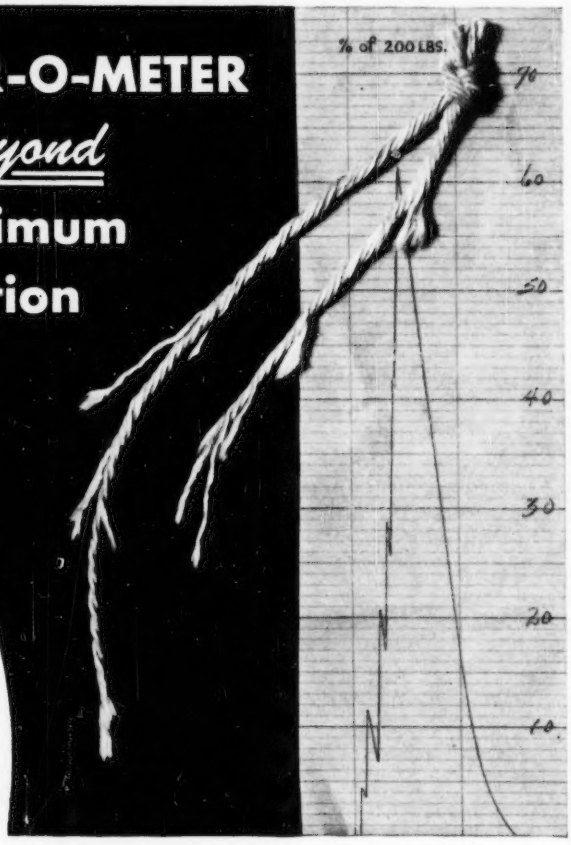

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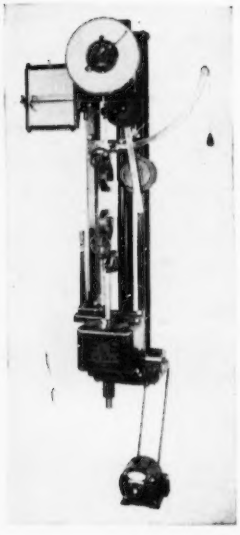

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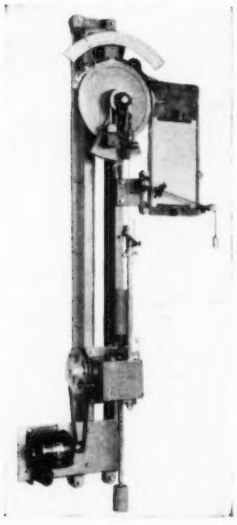

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TEXTILE RESEARCH JOURNAL

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The Prediction of Equilibrium Thermal Comfort from Physical Data on Fabrics*

H. B. Hardy, Jr., J. W. Ballou, and O. C. Wetmore

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Abstract

The effect of clothing on thermal comfort depends mainly on three factors: the physical properties of the fabric, the air spaces between the body and the fabric, or between the fabrics themselves, and the characteristics of the environment, such as its effective radiative temperature and the temperature, velocity, and relative humidity of the air. All these factors are considered in the development of a theory which permits, in principle, the prediction of the equilibrium thermal comfort associated with any fabric under any specified set of conditions, on the basis of "thermal resistivities" which may be measured with laboratory apparatus. The step-by-step solution of a typical problem concerning the relative comfort ratings of several fabrics is presented as an example of the method.

ONE of the many factors which determine the ultimate acceptance or rejection by the consumer of an item of clothing is its comfort; thus, a knowledge of how to make garments comfortable is highly important to the textile technologist.

The problem of analyzing the factors which influence comfort is complicated by the fact that this state of existence is not easy to define, and many of the variables which influence it are purely psychological. Therefore, this paper will deal only with *thermal* comfort, which can be defined as the absence of any unpleasant sensations of being too cool or too warm, or of having too much perspiration on the skin. This is a major factor in determining the degree of general comfort, and is one over which textile engineers have some control. Moreover, it is possible to describe in physical terms two factors which have been shown to be good indicators of thermal comfort —the temperature of the skin and the amount of moisture on it.

Studies have been and are being made of the influence of clothing on the physiological and, to some extent, the psychological reactions of human beings in controlled environments [1, 3, 4, 5, 6, 7, 8]. The present paper describes a method of using data obtained from laboratory equipment to predict the thermal comfort of any individual in thermal equilibrium with his environment, while wearing specified clothing under specified circumstances. The ultimate objective of this work is to provide quantitative rela-

* Presented in part at the Annual Meeting of Textile Research Institute, New York City, Nov. 18, 1952.

tions between the commonly measured physical properties of fabrics and their effects on equilibrium thermal comfort. These may then be used as bases for the logical design of clothing for maximum comfort.

General Background

The heat produced by the human body must be dissipated to its surroundings, and the body attempts to regulate the rate of heat loss so that it equals the rate of production, in order to maintain the internal organs and deep body tissues at a constant temperature. The body accomplishes this regulation mainly by varying the temperature of the skin (by dilating or constricting the capillary blood vessels near the surface), especially at the extremities, and by varying the amount of perspiration on the skin.

Of course, whenever the metabolism or the environmental conditions change abruptly, or when extra clothing is put on, this normal state of dynamic thermal equilibrium is temporarily upset. However, the body then reacts by readjusting the skin temperature and perspiration output in such a way as to restore the balance between heat production and loss. In other words, if the degree of activity does not change, putting on extra clothing does not result in a permanent reduction in the rate of heat loss from the body, but rather in increased skin temperature or skin wetness, or both.

About 90% of the heat produced by the body is dissipated from the surface of the skin, by conduction, convection, radiation, and the evaporation of perspiration ([5], p. 116). The other 10% is carried away in the warmed, exhaled breath and other bodily secretions (including perspiration which drips off the body).

The heat which is dissipated from the surface of the skin must, of course, pass through the layers of clothing which normally surround the body. The major function of this clothing, from a thermal standpoint, is to maintain the layers of air next to the skin relatively motionless; it is these layers of semistagnant air which actually provide most of the insulation. Therefore, the effect of a fabric on thermal comfort cannot be determined accurately by merely measuring the amount of insulation between the two fabric surfaces. The way in which the fabric influences the adjacent air layers, particularly those between the fabric and the skin, is an important factor, and must be considered.

The influence of the fabric on these semistill layers of air around the body depends to a large extent on such factors as the style and fit of the garment and the kind of weather in which it is worn—for example, windy or calm. It is therefore impossible to draw accurate general conclusions about the relative comfort ratings of several fabrics on the basis of tests made with only one type of garment in only one kind of environment. It will be shown below that the relative warmth ratings of two fabrics under a given set of conditions may actually be reversed under another set of conditions.

We find, in other words, that the comfort properties of fabrics can be assessed and compared accurately only in terms of specific, individual cases, each one involving a definite type of garment and some definite set of circumstances. For example: Will an average man be most comfortable while working at a specified steady rate, indoors, with a constant, definite ambient air temperature and relative humidity, if he is clothed in single-layer coveralls made of fabric *A*, fabric *B*, or fabric *C*? This paper describes a procedure for answering such questions, which deal with an individual in thermal equilibrium with his surroundings, on the basis of data obtained with laboratory equipment. The method is based, first, on the physical laws of heat transfer, and, secondly, on physiological data concerning the relation between skin temperature, perspiration, and thermal comfort.

Heat Transfer from the Skin

Heat can be dissipated from the surface of the skin only if there is some "driving force" to cause it to flow through the surrounding insulation. Four such driving forces are possible—namely: (*1*) a difference between the temperature of the skin and that of some other solid body immediately adjacent* to it $(T_s - T_b)$; (*2*) a difference between the temperature of the skin and that of the ambient air $(T_s - T_a)$; (*3*) a difference between the temperature of the skin and that of the surrounding walls or other radiative environment $(T_s - T_w)$; (*4*) a difference between the vapor pressure of the perspiration on the skin and that of the water in the ambient air $(E_s - E_a)$. If any of these driving forces are negative, they will, of course, cause heat to flow *to* the body, rather than from it.

If Q_1 represents the rate at which heat will leave the body due to the first driving force $(T_s - T_b)$,

* That is, in contact or separated only by the clothing worn.

and Q_2, Q_3, and Q_4 are similarly defined, then the total rate at which heat will be dissipated from the skin surface due to all causes will be

$$Q = Q_1 + Q_2 + Q_3 + Q_4. \qquad (1)$$

The rate at which heat flows is proportional in each case * to the driving force which causes it to flow, so that equation (1) can be extended as follows:

$$\begin{aligned} Q &= Q_1 + Q_2 + Q_3 + Q_4 \\ &= \frac{1}{P_1}(T_s - T_b) + \frac{1}{P_2}(T_s - T_a) \\ &\quad + \frac{1}{P_3}(T_s - T_w) + \frac{1}{P_4}(E_s - E_a). \qquad (1a) \end{aligned}$$

Note that the driving forces are not necessarily equally effective in causing heat to flow—that is, the proportionality coefficient, $\frac{1}{P}$, may be different for each driving force, as denoted by the subscripts.

The rate at which heat will be lost from the skin due to any given driving force will also be proportional to the area of skin which is subjected to the driving force. Therefore,

$$\begin{aligned} Q &= A_b\frac{(T_s - T_b)}{\rho_1} + A_a\frac{(T_s - T_a)}{\rho_2} \\ &\quad + A_w\frac{(T_s - T_w)}{\rho_3} + A_e\frac{(E_s - E_a)}{\rho_4}, \qquad (1b) \end{aligned}$$

where A_b is the area of the skin which is in contact † with other solid objects, A_a is the area of the skin exposed † to the ambient air, A_w is the area of the skin which can "see" † (and thus radiate to) the surrounding radiative environment, and A_e is the area of *wet* skin exposed † to the ambient air. The factors ρ_1, ρ_2, ρ_3, and ρ_4 are, of course, merely P_1A_b, P_2A_a, etc.

The area A_e can be expressed as wA_a, where w is the fraction of the skin area exposed to the ambient air which is also *wet*. Gagge [3] has called this quantity the "wetted area," and has defined it precisely as the "area of water at skin temperature which would yield the evaporation actually observed," expressed as a fraction or percentage of the "maximum possible wetted surface of the body." Actually, of course, one never finds a certain fraction of his skin area dripping with sweat and the remainder bone dry. The entire area of the skin is always more or less moist with perspiration. (Even when the skin seems dry, there is some secretion of "insensible perspiration," which evaporates as soon as it reaches the surface.) However, an area of skin which is merely moist cannot dissipate heat by evaporation as fast as if it were totally covered with water, so that, as far as heat loss rates are concerned, the effect is exactly the same as if some fraction, w, of the skin area were totally wet and the rest were completely dry. Thus, the factor w is quite useful in describing *how wet* the skin is, on the average; for this reason, it will be called *skin wettedness* in this paper.

The solution of equation (1*b*) can be simplified by the use of the relationship

$$E_x = \frac{e^{.0553T_x}}{1.68}, \qquad (2)$$

where E_x is the saturated vapor pressure of water at temperature T_x. This relationship was derived empirically from a plot of E_x *versus* T_x, and is accurate to $\pm 2\%$ in the temperature range from 20°C to 50°C. Since the vapor pressure of the perspiration on the skin may be assumed to be equal to the saturated vapor pressure of water * at skin temperature, and since the vapor pressure of the water in the air is equal to its saturated vapor pressure at the temperature of the air multiplied by the relative humidity (R.H.), the equation for the total rate of heat loss from the surface of the skin may finally be written

$$\begin{aligned} Q &= A_b\frac{(T_s - T_b)}{\rho_1} + A_a\frac{(T_s - T_a)}{\rho_2} + A_w\frac{(T_s - T_w)}{\rho_3} \\ &\quad + wA_a\frac{(e^{.0553T_s} - (\text{R.H.})e^{.0553T_a})}{1.68\rho_4}. \qquad (3) \end{aligned}$$

Thermal Resistivities

The heat flow rates Q_1, Q_2, etc., in the equations above can be considered analogous to current in an electrical circuit, while the thermal driving forces are analogous to the potential differences, or voltage drops, which cause the current to flow. An inspection of equation (1*a*) will show, then, that the quantities P_1, P_2, P_3, and P_4 are analogous to electrical resistances; and they are therefore called *thermal* resistances.

* Actually, $Q_3 \propto (T_s^4 - T_w^4)$, where the temperatures are given in absolute degrees. Since the differences between T_s and T_w are always small compared to their absolute values, $(T_s^4 - T_w^4)$ may be approximated by $4T_s^3(T_s - T_w)$. Normal variations in T_s are quite small compared to its absolute value, so that, essentially, $Q_3 \propto (T_s - T_w)$.

† In case the body is clothed, the clothing must be ignored in applying these definitions. That is, A_b is then the area of skin which *would* be in contact with other solid objects if it were not for the intervening clothing, and so on.

* This is not strictly correct, since the vapor pressure of perspiration is lowered slightly by its salt content. This is accounted for, however, in the factor w, as defined by Gagge.

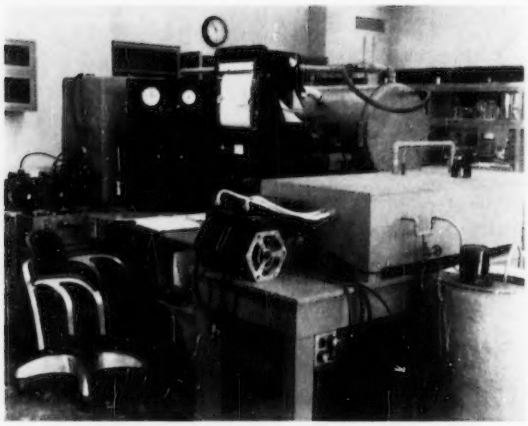


FIG. 1. *Apparatus for measuring thermal resistivities, showing control panel.*

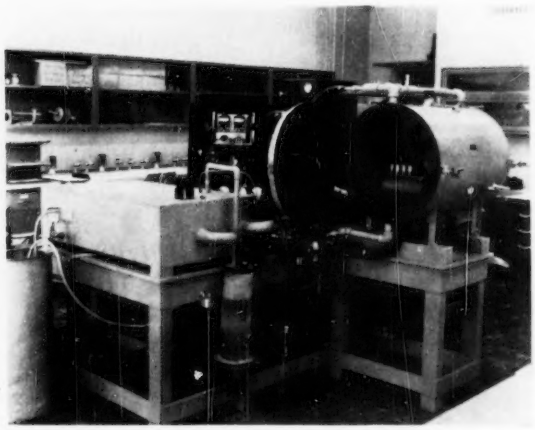


FIG. 2. *Apparatus for measuring thermal resistivities, showing controlled-environment chamber.*

Since ρ_1, ρ_2, etc., are simply these same thermal resistances expressed in terms of the heat flow from unit area of the skin, they have been termed *thermal resistivities*. These quantities are measures of the amount, or effectiveness, of the insulation through which heat must flow in order to leave the body. Therefore, with the exception ρ_1 (which is defined only for areas where the fabric is pressed against the skin and shielded from the ambient air by some solid object), the thermal resistivities associated with any given fabric are *not* constants. They depend, as previously indicated, on such factors as the "air gap" (distance from the skin to the fabric) and wind speed, as much as on the physical properties of the fabric itself. It is possible, however, to measure ρ_2, ρ_3, and ρ_4 in the laboratory as functions of most of the variables which affect them.

Measurement of Thermal Resistivities

The apparatus used to measure thermal resistivities is shown in Figures 1 and 2. It consists basically of a guarded hot plate (Figure 3), simulating a section of the surface of a human body, which can be covered with fabrics and then subjected to a variety of environmental conditions. Provision is made for controlling and measuring nearly all the factors which might possibly influence the rate of heat loss from the simulated skin.

This "skin" is, in reality, a 4-in. square section of chamois supported by a thin, perforated copper plate over a very shallow copper pan. The chamois is kept saturated with water which penetrates the perforated plate from the pan below. Distilled water is supplied to the pan through a small copper tube (visible in the foreground of Figure 3) which makes a complete circuit under the independently heated guard ring before emptying into the pan, in order to preheat the water to the temperature of the chamois surface. A constant-level device automatically adjusts the rate of feed so that it equals the rate at which the water is evaporated from the chamois.

For measurements involving a dry skin, a second guarded hot plate is used. It is similar to the one illustrated except that the center plate, or skin, is simply a copper plate painted flat black, like the guard ring, to match the essentially black-body infrared radiation characteristics of the human body ([5], p. 81).

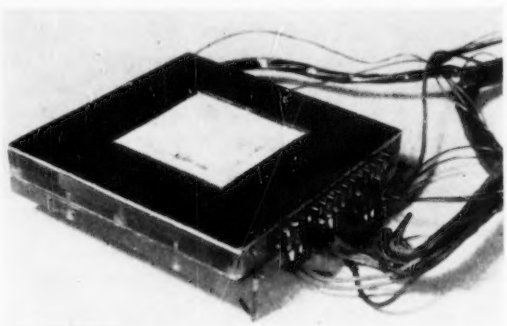


FIG. 3. *Simulated perspiring skin, showing arrangement of guard ring and bottom plate.*

The skin can be automatically maintained at any desired temperature between about 30°C and 60°C. Heat is supplied electrically through lengths of *Nichrome* resistance strip wound on $\frac{1}{16}$ in. thick *Bakelite* resin forms. Temperature control is accomplished by the use of two thermistors situated just under the heated surface and connected electrically to opposite arms of an alternating-current bridge. This bridge is balanced at the desired temperature by means of a variable resistor in the third arm, mounted on the control panel. Any deviation of the temperature from the value selected produces an unbalance signal from the bridge, and this is amplified and used to operate a relay which increases the voltage applied across the heater by a certain percentage. The base voltage can be varied by means of a control mounted on the panel.

The temperatures of the guard ring and bottom plate (which covers the entire area underneath the center plate and guard ring) can also be automatically and independently controlled. When all the plates are at the same temperature, heat supplied by the center plate heater can be dissipated only from the outer surface of the skin. Thus, under this condition of thermal equilibrium, the rate at which heat is lost from the skin can be determined simply by measuring the electrical power supplied to its heater.

The hot plate is mounted inside a cylindrical environmental chamber, beneath the flat area of fabric seen in Figure 4. The walls of this chamber are water-jacketed, and can be maintained at a predetermined temperature to simulate any desired radiative environment except direct exposure to sunlight or other short-wave-length radiation. Air can be blown at the test fabric, normally, at 45°, or at grazing incidence, through slits in the chamber wall, one of which is barely visible in Figure 4. The temperature and relative humidity of this air are controlled, independently of the wall temperature, by an air conditioner located outside the chamber. The air speed (at the hot plate surface) can be varied from about 1 to 5 m.p.h.

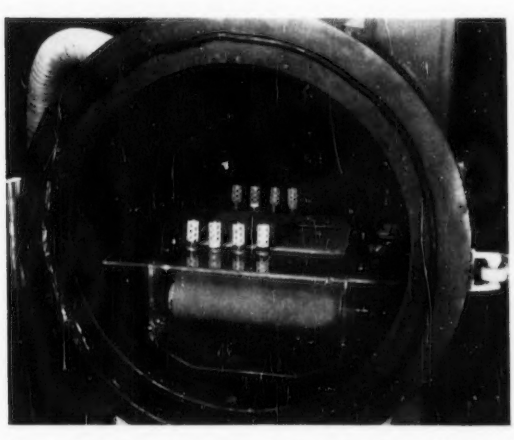


FIG. 4. *Interior of environmental chamber. The small cylindrical objects are humidity-sensing elements.*

Fabrics to be tested are fastened end to end to form a scroll which is conditioned in the selected environment on a spool, shown in the foreground of Figure 4. The fabrics can be cranked over the hot plate, one at a time, for testing, in the same way that film is rolled into place in a camera, without opening the doors of the chamber or in any way disturbing the test environment. The air gap between the fabric and the skin can be varied by raising or lowering the hot plate. The fabrics are held under a slight constant tension, not enough to deform them appreciably, but sufficient to keep them from sagging when not supported by the plate.

The temperatures of the skin, guard ring, bottom plate, chamber walls, air, etc., are all measured with copper-constantan thermocouples and recorded automatically. The air speed near the surface of the hot plate is measured with a hot-wire anemometer, and sensing elements of the Dunmore type are used to measure and control the relative humidity of the air inside the chamber.

The four thermal resistivities can be measured separately and independently by adjusting the environmental conditions in the chamber so that only one driving force exists at one time, and then calculating the resistivity associated with that driving force from measurements of the resulting rate of heat loss. For example, if the dry, copper skin is used, so that $w = 0$, and if it is not covered with any solid object, so that $A_h = 0$, and if the wall temperature is maintained equal to the skin temperature, so that $(T_s - T_w) = 0$, then equation (3) reduces to

$$Q = A_a \frac{(T_s - T_a)}{\rho_2},$$

and ρ_2 may be calculated from measurements of T_s, T_a, the resultant rate of heat loss, Q, and A_a (which, of course, equals the total area of the center plate). Resistivities ρ_3 and ρ_4 are calculated in an analogous manner. In measuring ρ_1, the wet, chamois center plate is used, so that $w = 1$. Air and wall tempera-

tures are both maintained equal to the skin temperature, and equation (3) reduces to

$$Q = A_a \frac{(e^{.0553T_s}(1 - \text{R.H.}))}{1.68\rho_1}.$$

Thermal resistivity ρ_1 can be measured with this apparatus by supporting some solid, constant-temperature object (such as a pan of melting ice) directly on top of the fabric covering the hot plate. As has been indicated, however, ρ_1 is essentially a constant for each fabric; it can be shown, in fact, that

$$\rho_1 = A_b \frac{(T_s - T_b)}{Q} = \frac{L}{k},$$

where L is the thickness of the fabric and k is its thermal conductivity. Since these two factors can be measured with simpler devices, the apparatus described here is seldom used to measure ρ_1.

The three resistivities ρ_2, ρ_3, and ρ_4 can be measured for each fabric under a variety of conditions of air gap, wind speed, and angle of incidence. The results are usually expressed in graphical form. It is then possible to read from these curves the values of the thermal resistivities which would be associated with that fabric under any set of conditions which might be of interest—for example, those in the illustrative case described below.

Equilibrium Physical Curves of T_s versus w

As an example of the application of equation (3) to specific situations, consider now the following question: Will an average man be most comfortable while working at a steady rate of 70 watts, indoors, with a constant ambient air temperature, T_a, of 86.3°F (30.2°C) and a relative humidity of 42%, if he is clothed in single-layer coveralls made of fabric A, fabric B, or fabric C? The ambient air conditions chosen here are those of an average July day in Philadelphia. It is reasonable to assume that on such a summer day, with windows open, the walls of the room in which the individual is to work would be at the temperature of the ambient air (that is, $T_w = 30.2$°C), and that the rate of air movement in the room would be about 1.5 m.p.h.

Before proceeding to calculate the comfort ratings of the three fabrics under these conditions, it would be well to establish a base line, by first considering the thermal comfort of the individual in the nude. Data which have been obtained from the laboratory equipment indicate that, for nude skin exposed to a 1.5 m.p.h. wind, $\rho_2 = 392 \pm 6$°C/w./sq. cm.; $\rho_3 \cong$ 1600°C/w./sq. cm.; and $\rho_4 = 24.8 \pm 2.3$ cm. Hg/w./sq. cm.

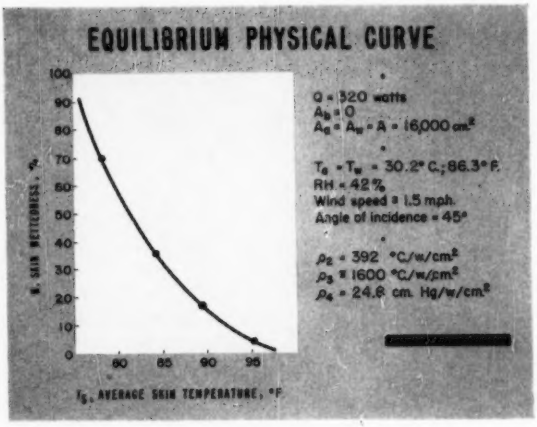


FIG. 5

The total skin area of any individual can be estimated by measuring his height and weight and substituting into a formula proposed by DuBois ([8], p. 18). In the case under consideration here, the subject will be assumed to have a total skin area of 16,000 sq. cm. Let us assume further that he would be standing at his work, and thus touching other solid objects only at the soles of his feet and the palms of his hands. A_b, in equation (3), can then be considered essentially equal to zero, and the entire first term on the right side of the equation vanishes. If $A_b = 0$, A_a will be very nearly equal to the total area; and, for simplicity in calculation, A_w will also be assumed to be 16,000 sq. cm. (Actually, A_w will always be somewhat less than the total skin area, because of the areas of the body, like the armpits, which can "see" only adjacent areas of the same body. This reduction in A_w varies from 15% to 30% of the total area, depending on the position of the body ([5], p. 85).

When all these data have been substituted into equation (3), only three unknown quantities remain —Q, T_s, and w. It is known, moreover, that the body's regulatory mechanisms continually and automatically adjust the last two parameters, T_s and w, in an attempt to maintain the total rate of heat loss equal to the rate of heat production, or metabolism. Since this paper deals only with those cases in which this equality exists, Q, the rate of heat loss from the skin, may be estimated from a knowledge of the metabolic rate

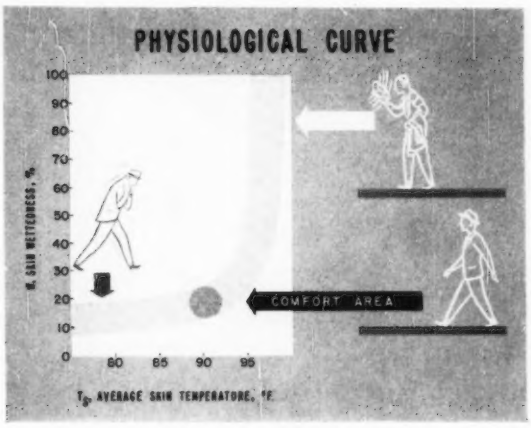


FIG. 6. *The boundaries of the shaded band are formed by the hyperbolas* $(36–T_s)$ $(w–0.15) = 0.41$ *and* $(38–T_s) \times (w–0.05) = 0.49$. *These equations are completely empirical.*

The metabolism of the average person has been found, in tests on large numbers of human subjects [8], to be about four times the rate at which work is being done, plus the basal metabolism, which averages about 40 kg.-cal./hr./sq. m. of skin area for males 25 years of age. Thus, the metabolism of the individual under consideration could be assumed to be 4 times 70 watts plus 75 watts basal metabolism, or 355 watts; and Q (under equilibrium conditions) would be about 90% of this, or 320 watts.

The only unknown quantities now remaining in equation (3) are T_s and w, and the equation can be solved for w as a function of T_s to yield the *equilibrium physical curve of skin temperature* versus *wettedness* for the particular set of conditions under consideration (Figure 5). The significance of this curve is simply that, if this particular individual is to maintain his thermal equilibrium while doing useful work at the rate of 70 watts, in the nude, under the environmental conditions which have been assumed, then the physical laws of heat transfer demand that he would have to exhibit some combination of skin temperature and wettedness which can be represented by some point on the curve. The general slope of the curve reflects the fact that at lower values of T_s, w must be greater, so that increased evaporation will make up for decreased heat losses by convection and radiation, and the total rate of loss will remain equal to the metabolic rate. Any change in the conditions of the case, such as clothing the individual in various garments or changes in the environment or rate of doing work, will, of course, lead, in general, to a different solution of equation (3)—that is, to a different physical curve of T_s *versus* w.

The Physiological Curve of T_s *versus* w

If either T_s or w could now be predicted independently, the other would be fixed by the physical curve. Ordinarily, however, the actual combination of T_s and w which would be observed under the assumed conditions depends upon the physiological responses of the individual. Although these vary to some extent from person to person and from day to day, considerable information is available on the *average* physiological behavior of the body in response to varying skin temperatures.

It is a matter of common experience, for example, that one does not sweat profusely when his skin temperature is low. Extensive experiments [3] have shown that when T_s is below about 86°F (30°C), skin wettedness (due to perspiration) seldom exceeds 20%. On the other hand, w almost never falls below about 10%, even in cold environments, due to continual insensible perspiration. As skin temperature rises above about 89°F, however, one begins to perspire more freely, and by the time T_s reaches 95°F (35°C), profuse sweating begins, in an attempt to cool the skin by evaporation. Skin temperature rarely rises above 96°F without the body becoming dripping wet with sweat—that is, $w = 100\%$.

These facts can be represented by a *physiological curve of skin temperature* versus *wettedness*, which, due to individual variations in physiological response, is actually a band (Figure 6). Under normal conditions (when physiological response is a controlling factor), the *equilibrium point* (the combination of T_s and w which would actually be observed) for any subject under any set of conditions will always lie somewhere within this band.

Predicting Thermal Comfort

It is possible, then, to predict that the individual under consideration, working in the nude at a rate of 70 watts under the environmental conditions assumed, would exhibit a combination of skin temperature and skin wettedness which is represented by a point at (or within) the intersection of the physical curve for that particular situation (Figure 5) and the physiological curve (Figure 6). This intersection is illustrated in the left-hand graph (for July) in Figure 7. This graph also shows the physical curves

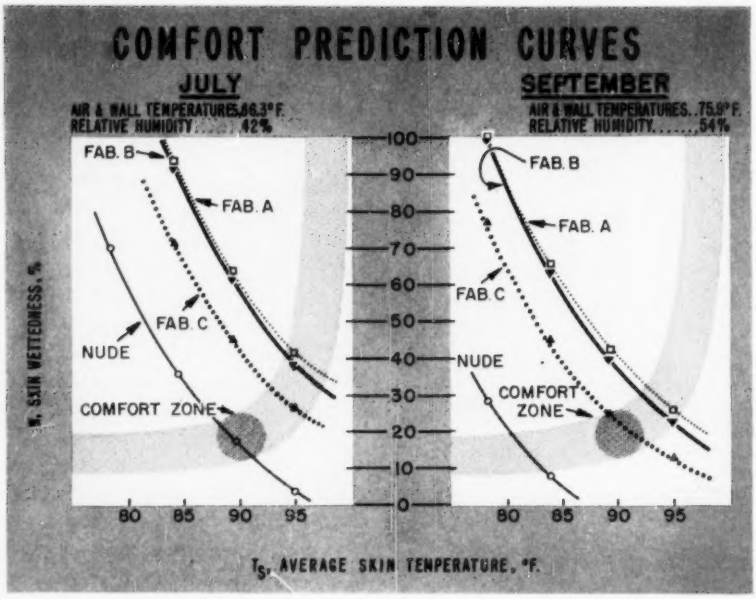


FIG. 7. *$Q = 320$ watts, $A_b = 0$, $A_a = A_w = 16{,}000$ cm.², wind speed = 1.5 m.p.h., angle of incidence = 45°, and air gap between "skin" and fabrics = ¼ in.*

which result from the assumption that the individual is clothed in a single-layer coveralls made from fabrics *A*, *B*, and *C*, respectively. The curves in the right-hand graph are based on the assumption of the meteorological conditions of a typical September day in Philadelphia ($T_a = T_w = 75.9°F = 24.4°C$ and R.H. = 54%), all other conditions being the same as in the July case.

These curves are based on thermal resistivities measured for three actual fabrics, whose physical properties are shown in Table I. These fabrics were not chosen with any intention of comparing cotton, nylon, and wool on an equal basis, but because they represented three quite different types of fabric, which might be expected to affect thermal comfort in different ways. The thermal resistivities used in the calculation of these curves were measured with a ¼-in. air gap between the fabrics and the simulated skin, on the assumption that this is approximately equal to the effective average air gap under conventional coveralls. The significance of this assumption will be discussed later.

It is well known that one is uncomfortable when he is chilly, or when he is "sticky" because of too much perspiration on his skin. Following an extensive series of experiments with four subjects, covering a period of almost two years, Winslow, Herrington, and Gagge [7] concluded that the two factors T_s and w were the only physiological variables which could be strongly correlated with subjective impressions of thermal comfort or discomfort. Their experiments showed that when the subjects' skin

TABLE I. PHYSICAL PROPERTIES OF FABRIC SAMPLES

Code letter	Description	Weave	Construction (ends×picks)	Yarn count	A.S.T.M. thickness (cm.)	Weight (g./cm.²)	Density (g./cm.³)	Air permeability (ft.³/min./ft.² per ½ in. water)
A	Cotton shirting	Plain	68×60	38/1 c.c.	.028	.0123	0.439	44
B	Continuous filament nylon shirting	Plain	108×88	79 denier	.013	.0071	0.551	67
C	Women's dress goods of 80/20 wool/*Orlon**	2×1 Twill	35×23	7/1 c.c.	.079	.0199	0.254	178

* DuPont's trade-mark for its acrylic fiber.

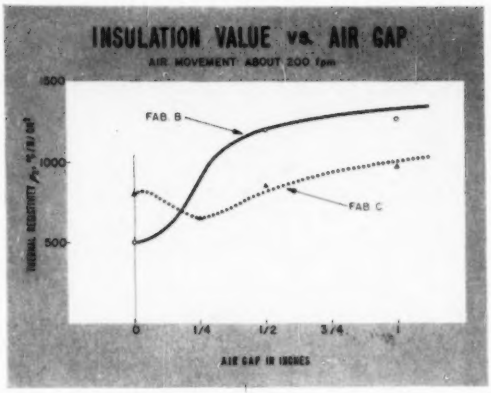


FIG. 8. *Values of ρ_z at ¼-in. air gap shown here were used in calculating the physical curves in Figure 7.*

temperatures were between 88°F and 92°F (with wettedness correspondingly low), they were almost invariably comfortable. This *comfort zone* has been indicated in Figures 6 and 7. As skin temperatures dropped below 88°F, the subjects' discomfort increased in direct proportion to the decrease in T_s. Skin wettedness seemed to have very little effect on comfort in this range of skin temperatures—a fact not difficult to understand when one notes (Figure 6) that w is low and almost constant for all skin temperatures below 88°F. As skin temperatures rose above 92°F, on the other hand, discomfort increased linearly with skin wettedness, with T_s exhibiting a somewhat lower degree of correlation with comfort.

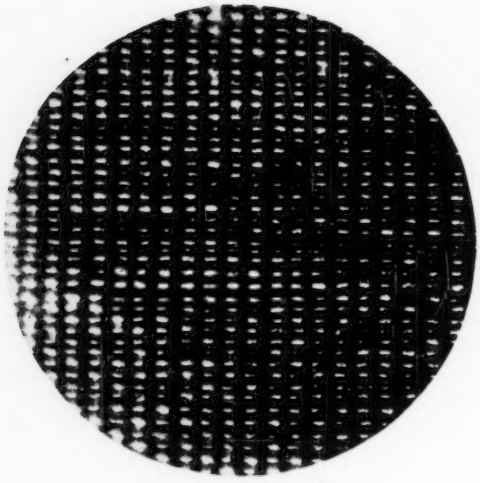
In short, an individual's thermal *dis*comfort is roughly proportional to the distance along the physiological curve from the comfort zone to the equilibrium point (intersection with the physical curve) for any given situation. Therefore, the illustrative question can now be answered as follows: In July, under the conditions of wind speed, air gap, etc., which have been assumed, this individual would be somewhat more comfortable in coveralls of fabric *C* than of either fabric *A* or *B*, although he would be most comfortable (thermally) in the nude. In September, on the other hand, he would be uncomfortably chilly in the nude, comfortable in fabric *C*, and slightly warm in fabric *A* or fabric *B*.

Discussion of Results

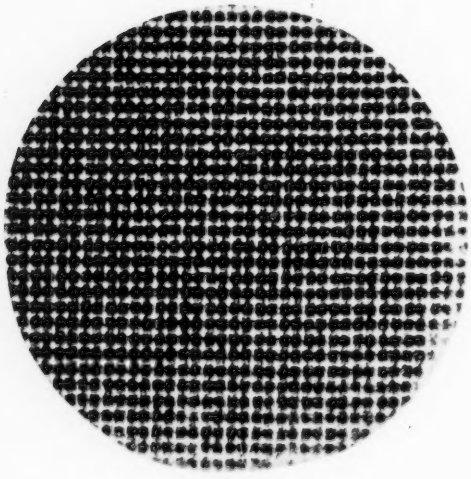
Figure 7 indicates that fabric *C* would be the most comfortable of the three fabrics under consideration, even though it is relatively thick and heavy, whereas fabrics *A* and *B*, which are "warmer" according to Figure 7, are light, thin shirtings. This somewhat unexpected result illustrates the marked effect of porosity and air gap on the insulation associated with these (or any other) fabrics. Figure 8 shows the variations in one of the four thermal resistivities (ρ_z) associated with fabrics *B* and *C*, respectively, caused by varying the distance between the fabric and the simulated skin of the measuring instrument. (The curve for fabric *A* is very similar to that for fabric *B*.) Note that when the fabrics are in contact with the skin (air gap = 0), the higher insulation value (to heat lost by virtue of driving force number two) is associated with the thicker, heavier fabric *C*, as one would expect. When the fabrics are held away from the skin, however, fabric *B*, due to its relatively tight weave (see Figure 9) and consequent low air permeability (Table I), traps a layer of stagnant air next to the body, thus providing increased insulation. The more porous fabric *C*, on the other hand, allows the wind to penetrate, disturbing the layer of air which was previously held immobile by the presence of the fabric, thus actually decreasing the total insulation over a certain range of distance. (The dip in the curve for fabric *C* is even more pronounced at higher air speeds.) It is this effect which would cause the coveralls made from the thicker but more porous fabric *C* to be the "coolest" of the three, assuming that the effective average air gap between the fabrics and the subject's skin would be ¼ in.

Some preliminary investigations also have been made of the relationships between thermal resistivities and various fabric properties and environmental variables. The findings of previous investigators [2, 6] that rates of heat loss by convection and evaporation are linear functions of the square root of the air speed have been confirmed. Data obtained thus far also indicate that under normal conditions, when wind speed is at least 1 m.p.h. and air and wall temperatures are nearly equal, *thermal* comfort is not affected appreciably by differences in the long-wavelength infrared emissivities or the hygroscopic character of the fabrics, providing they are not actually wet.

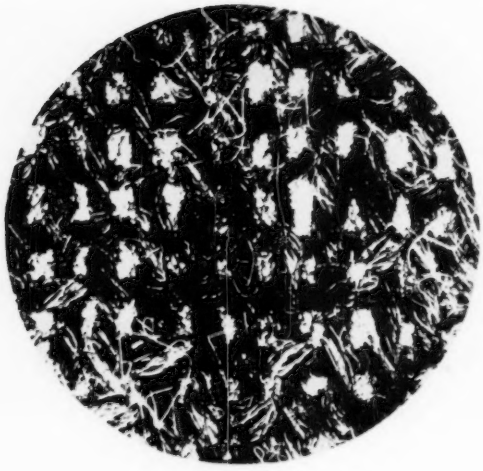
A number of refinements will be necessary in order to apply this method of predicting thermal comfort to problems involving conventional garments under a variety of actual conditions. The determination of the air gaps actually existing under



Fabric A



Fabric B



Fabric C

FIG. 9. *Photomicrographs taken at 8× magnification. Light transmitted from behind the fabrics reveals the relatively open structure of fabric C.*

various types of garments, when worn, is one of the next steps which must be taken. Much remains to be done in order to extend this approach to non-equilibrium cases in which the environment or the metabolism is not constant. Possible changes in the design of the chamber are being investigated with the objective of obtaining air-flow patterns which will more closely simulate the effect of actual winds striking the irregularly shaped human body. Information obtained with actual human subjects wearing conventional garments in controlled environments will be necessary in the solution of all of these problems.

Acknowledgment

The authors wish to acknowledge the assistance, in various phases of this work, of Dr. J. C. Smith and Dr. R. M. Hoffman of the Du Pont Company, and Dr. J. D. Hardy of the Cornell University Medical College.

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(Manuscript received November 10, 1952.)

Fabric Evaluations Based on Physiological Measurements of Comfort*

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Abstract

Physiological factors such as body surface temperature, electrical conductivity of the skin, rate of sweating, total sweat cost, and heart rate were measured as criteria for evaluating in warm and hot environments the comfort afforded human test subjects by textile apparel. To correlate the physiological parameters with individual impressions of comfort and to assess the contributing psychological factors, expressions of subjective opinion of the different fabrics were solicited.

IN the preceding paper [1] different textile fabrics were compared as to their performance in resisting the flow of heat emanating from an electrically heated surface representing the skin. The insulation values of the fabrics were then related to the possible comfort afforded by each in the light of established physiological measurements of skin temperature and wettedness. Although these thermal effects contribute extensively to the "comfort" of an individual, complex physiological and psychological factors collectively play an important role in defining this abstruse quality with reference to clothing. A better understanding of the influence of clothing on the human factors which determine the degree of comfort is the principal objective of this research. A major part of this study has been concerned with an investigation of the physiological responses to various stimuli provided by different textile fabrics being worn by human subjects under controlled climatic conditions.

The physiological factors chosen for exploration as criteria of comfort were: average skin temperature, the degree of skin wetness as indicated by electrical conductivity at the body surface, the rate at which the subject perspires, how much he perspires (*i.e.*, the total sweat cost), the amount of perspiration picked up by the garment during test, and the subject's body temperature and heart rate.

Laboratory Facilities

For comparisons of the comfort associated with different fabrics the environmental test conditions were carefully defined, and it was desirable that evaluations be carried out over a range of conditions. Essentially, these factors required a space in which air temperature, relative humidity, and air movement could be adjusted to satisfy the particular study at hand. In the test chamber, a room 14 ft. × 19 ft. × 10 ft., environmental conditions for the present study were restricted to the warm, humid regions of climate, with control of air temperature and relative humidity from 60° to 100°F and from 50% to 95%, respectively. The conditioning system provided turbulent air at 0.3 m.p.h., and, when desired, wind velocities up to 10 mi./hr. could be generated by a 24-in. pedestal fan placed near the test subject.

All recording instruments were housed in an air-conditioned control room adjacent to the test chamber; and between the rooms a sealed window and a speaker system provided for direct observation of the test and communication with the subject.

Test subjects were exercised on a bicycle ergometer (Figure 1) and a treadmill (Figure 2). Work output on the bicycle was controlled by pedaling at regulated speed against a constant load applied through an electromagnetic braking system. The work load provided by the treadmill was controlled by adjusting the speed of the endless belt (from 0 to 7 m.p.h.) and the grade to which it was inclined (0% to 12%*). The treadmill offers a customary, everyday form of exercise, and therefore is probably the more desirable machine for comfort studies.

* Presented in part at the Annual Meeting of Textile Research Institute, New York City, Nov. 18, 1952.

* By 12% grade is meant a rise of 12 ft. for each 100 ft. traverse in the horizontal plane.

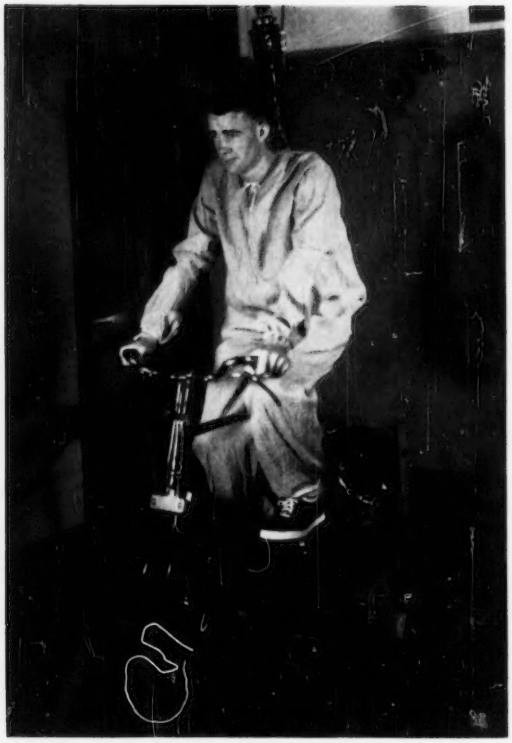


FIG. 1. *The testing of a whole coverall garment using a bicycle ergometer for exercise.*

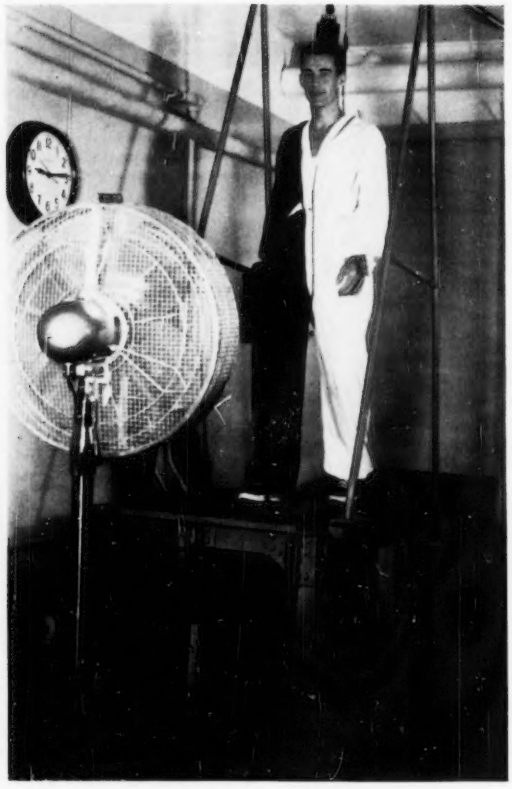


FIG. 2. *The testing of half-garments using a treadmill for exercise. Wind velocities were generated by the 24-in. pedestal fan.*

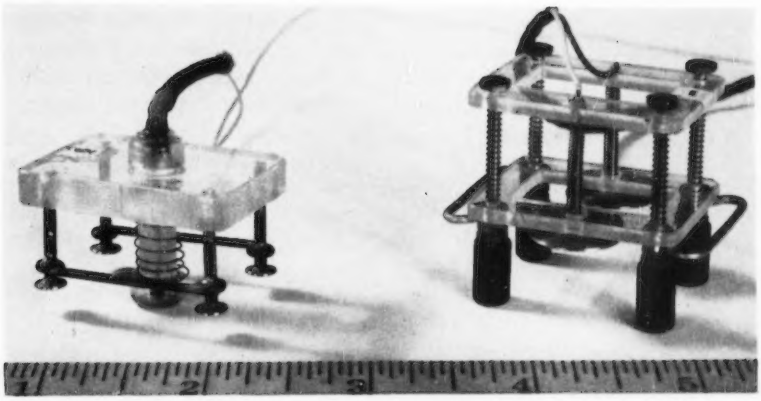
Instrumentation

Rather specialized techniques were necessary for measurement of the chosen physiological parameters, and to this end several new items of equipment and instrument modifications were developed. The following sections describe the principal measuring devices employed.

Skin Temperature

The temperature of the skin surface at given spot locations was measured by thermocouples of fine copper and constantan wire (36 gage), each of which formed an integral part of a temperature-sensing element (Figure 3). Each element consisted of a plate of *Lucite* acrylic resin, $1\frac{1}{4}$ in. $\times$ 1 in. $\times$ $\frac{1}{4}$ in., through which a plunger of *Lucite* moved freely. The plate was supported above the skin by four $\frac{3}{8}$-in. legs. The thermocouple junction was soldered to a $\frac{1}{4}$-in. diameter copper disk located at the end of the plunger. This plunger was equipped with a light tension spring which served to press the copper disk and thermocouple junction against the skin with an essentially constant pressure, irrespective of bodily movement and muscular activity of the subject. Such a spring-loaded system minimized temperature fluctuations resulting from change in contact pressure of the thermocouple against the skin. The copper and constantan lead wires were insulated with a nylon plastic sheathing, and the copper disc was coated with a thin layer of lacquer to prevent erroneous readings due to current leakage or short-circuiting.

Fourteen temperature-sensing elements were mounted in a harness of nylon tape which held the thermocouples in contact with the skin at various locations on the body surface. Figure 4 shows the manner in which the thermocouples were positioned symmetrically in pairs at the chest, back, forearms, stomach, thighs, calves, and near the ankles. Skin temperatures were recorded by the Brown instrument shown in the photograph. This instrument was



Skin temperature-sensing element. *Skin wetness-sensing element.*

FIG. 3

specially modified * to trace separately the curves of individual temperature variations with time at the different thermocouple locations. In addition, the recorder provided a continuous automatic average of skin temperature for each side of the body.

Skin Wetness

To follow variations in the amount of moisture on the surface of the body the electrical conductivity of the skin was measured using the second of the sensing elements shown in Figure 3. Actually, the electrical property measured was the resistance of the skin surface to the flow of current between the two plate electrodes. These values were then converted into conductivity units for graphing. Four skin wetness probes were positioned in the nylon harness so as to obtain skin conductivity at the thighs and on each side of the chest. When not in actual use, the electrodes were held away from the skin by springs located at the corners of the frame in order to prevent the accumulation of moisture and salt at the plate surfaces which would give rise to spurious resistance data. When conductivity measurements were desired, the electrode plates were made to contact the skin by having the test subject press the upper plate of *Lucite* toward the lower one against the spring tension. Contact pressure was controlled by spring windings at each electrode. The electrical circuit was completed through a simple ohmmeter which provided the current and measured electrical resistance as it varied with surface wetness. Release of hand pressure returned the electrodes to their original position.

New equipment just completed combines the tem-

FIG. 4. *Thermocouples and electrical conductivity units are shown at the positions where skin temperature and the degree of skin wetness are measured. Probes for recording heart rate are held by the black chest strap. Temperature recordings for each thermocouple are printed periodically on separate segments of the "roller towel" chart in the modified Brown instrument.*

* See Acknowledgment (p. 22).

perature and wetness units into one mounting, thus increasing from four to fourteen the positions at which conductivity will be measured. The electrodes will be controlled by the observer and activated mechanically by air pressure.

Sweat Cost

Test subjects were weighed frequently to determine sweat cost and the rate at which the individual perspired. The amount of moisture absorbed by the garments was also determined by weight change. Subject weighings were accurate to within ±5 g. and garment weighings to within ±1 g.

Heart Rate and Oral Temperature

Heart rate was recorded periodically by a cardiotachometer. Metal probes for this instrument were strapped around the chest (see Figure 4). Oral temperatures were determined with a precision clinical thermometer.

Evaluation of Experimental Procedures

Fabrics were tested in the form of single-layer, coverall-type garments which covered the body from the neck to the ankles (Figure 1); and the experimental routine was usually one of rest, exercise, and rest in the nude, followed by rest, exercise, and rest in one of the garments. Because body functions may vary to some degree from day to day, the nude part of the routine served as a control for each test and as a means by which the subject could adjust to the experimental conditions preparatory to the evaluation of clothing.

To assess properly the instrumentation and test procedures outlined above, three individuals were exposed to four different conditions of warm environment; and average skin temperature, skin conductivity, and heart rate were measured simultaneously throughout the test routine. Figure 5 shows the influence of environment on average skin temperatures at six representative points of time. As the severity of the environment increased, the average skin temperatures increased in clearly distinguishable increments. Furthermore, in any one of the four environments, skin temperature increased approximately 1°F in proceeding from the nude to the clothed situation. These variations indicated that average skin temperature is a sensitive parameter capable of distinguishing relatively small environmental changes and differentiating rather clearly the nude and clothed states. The uppermost curve is incomplete because the subject was excused from one of the two exercise periods due to the extreme environmental conditions (95°F, 90% R.H.). With the exception of the one experiment in which the subject was exposed to a 9 m.p.h. wind, air velocity was less than 1 m.p.h.

An increased capacity for electrical conductivity at the body surface has been associated with an accumulation of moisture on the skin; and, for the great majority of subjects tested, increasing skin wetness was associated with increasing discomfort. The effect of different environmental conditions on electrical conductivity of the skin or degree of skin wetness is shown in Figure 6.

Electrical conductivity increased with increasing air temperature and humidity, and for a given en-

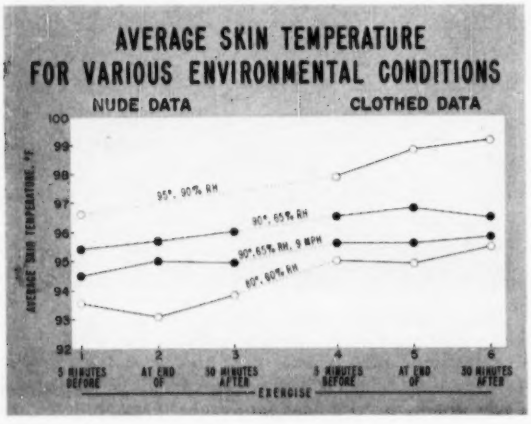


FIG. 5

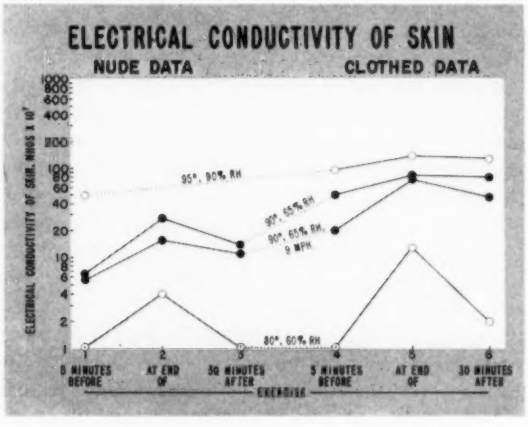


FIG. 6

TABLE I. FABRIC PROPERTIES

No.	Fabric	Fabric count	Weight (oz./yd.²)	Thickness (cm.)	Fabric density (g./cm.³)	Bending length (cm.)	Flexural rigidity (mg.-cm.)
1	80/20 wool/*Orlon* acrylic fiber	35×23	5.89	.079	0.254	1.52	77.0
2	Cotton shirting	68×60	3.62	.028	0.439	1.49	40.7
3	Filament nylon shirting	108×88	2.10	.013	0.551	1.66	32.6
4	Cotton denim	68×48	5.85	.048	0.412	1.64	88.0
5	Spun nylon denim	63×37	4.46	.046	0.330	1.25	29.4
6	Neoprene-coated nylon	108×96	3.38	.018	1.13	1.58	79.8

vironment, skin wetness increased when the test garment was put on. The curves also reflect the more profuse sweating experienced during exercise and the drying of the skin surfaces in the periods of rest which followed. Thus, the measurement of skin conductivity appeared to distinguish satisfactorily between different environments and between the nude and clothed situations.

Figure 7 shows that heart rate measurements distinguished moderately well the different levels of stress imposed on the subject by various atmospheric conditions; and, as expected, the heart beats more rapidly during periods of physical activity. However, under the prescribed conditions of test, only small changes were observed which could be attributed to additional stress provided by a single layer of clothing. Therefore, it was concluded that heart rate measurements provided a less sensitive criterion of comfort under these particular conditions than did either skin temperature or conductivity measurements. In later work it was evident that significant differences in heart rate could be obtained by wearing garments which were uncomfortable in the extreme.

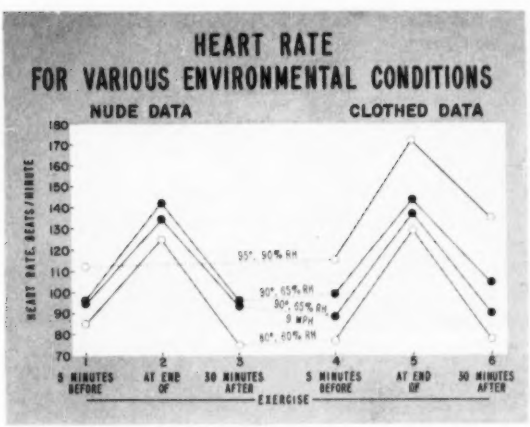


FIG. 7

Objective Fabric Evaluation

With methods established for measuring parameters sensitive to changes in human physiology, an evaluation of clothing comfort was initiated. First compared were three fabrics chosen for test not on a scientific basis, such as fabrics of equal thickness, but rather with the expectation that they would differ markedly in their influence on the selected physiological variables. Coverall garments were fashioned from commercial nylon and cotton shirting materials, and a medium-weight dress goods of 80% wool and 20% *Orlon* acrylic fiber. Relative fabric thickness is represented by the ratio 1:2:6 for nylon, cotton, and wool/*Orlon*, respectively (Table I, fabrics *1*, *2*, *3*). The thermal insulating properties of these materials were characterized by methods described in the preceding paper [1].

Figure 8 shows a typical comparison of average skin temperatures obtained in wearing the coveralls of cotton and wool/*Orlon* in an environment of 85°F and 50% R.H. The curves represent the average of data from duplicate tests performed by the same subject wearing each of the fabrics. The skin temperatures recorded during the initial rest periods reflect day-to-day physiological variations. The decrease in average skin temperature during exercise was attributed to the increased heat loss by convection and to a more rapid evaporation of perspiration by the increased air movement due to body motion. Another factor contributing to this surface cooling may be a decrease in the volume of blood supplied to the periphery attended by an increased flow to the working muscles ([4], p.283). As frequently observed during the second rest period, exercise had served to stabilize average skin temperature at nearly the same level in each test before the subject put on the test garment. The preliminary routine, therefore, served from day to day as a stabilizing test control and provided a basis for interpretation of the temperature variations which occurred in the latter

half of the experiment directly related to interfabric comparison.

Garments of both cotton and wool/*Orlon* acrylic fiber raised the level of average skin temperature (Figure 8), but the body surface of this particular subject became warmer under the wool/*Orlon* by about 0.7°F. This is only a small difference on the Fahrenheit scale, but with respect to normal variations in skin temperature it may prove to be significant as the number of tests increases. The cotton fabric and that of wool/*Orlon* were compared in tests of five individuals, three of whom attained higher surface temperatures under wool/*Orlon*, whereas no temperature differences were observed in the other two cases.

The skin conductivity data recorded during the same comparison of the cotton and wool/*Orlon* are shown in Figure 9. Definitely higher conductivities were observed in the second half of each test; and although the curve for the wool/*Orlon* attains a higher maximum, the differences will not be considered significant unless the data are confirmed by the new equipment capable of measuring conductivity at numerous other body locations.

The cotton and nylon shirtings were similarly compared; the graphs of average skin temperature and conductivity are shown in Figures 10 and 11. The curves for the two fabrics were essentially superimposable, and confirmation of the identical behavior was obtained on a number of other subjects. In no case could the fabrics be distinguished in a warm environment by evidence based on significant differences in temperature and conductivity at the surface of the skin.

The similar effects produced in wearing the two shirting materials were predicted by the physics laboratory testing [1]. However, in comparing the wool/*Orlon* with either the cotton or nylon, the predicted behavior [1] appeared not to be in accord with results obtained in physiological testing. Under certain conditions the loosely woven fabrics of wool/*Orlon* should have been "cooler" than the more tightly woven shirtings; but, as already shown in the environmental laboratory, the wool/*Orlon* tended to produce a higher skin temperature. The apparent discrepancy was associated with differences in experimental conditions—*viz.*, degree of air movement and width of air gap between fabric and skin. Wind speeds were 1.5 and 3.0 m.p.h. in the small physical test chamber, whereas the environmental laboratory provided only 0.3 m.p.h. air movement.

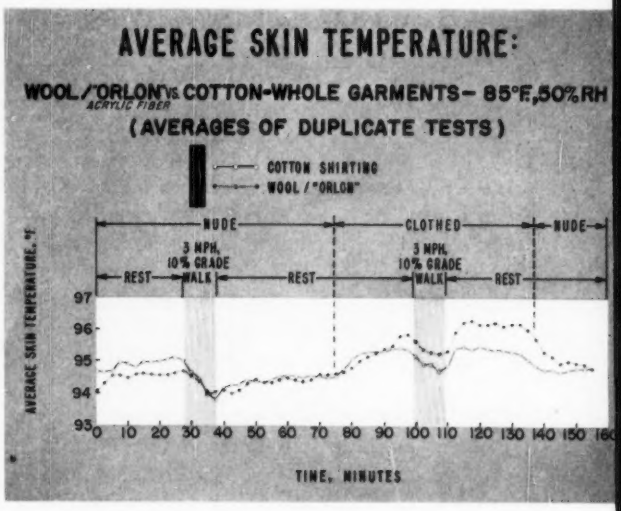


FIG. 8

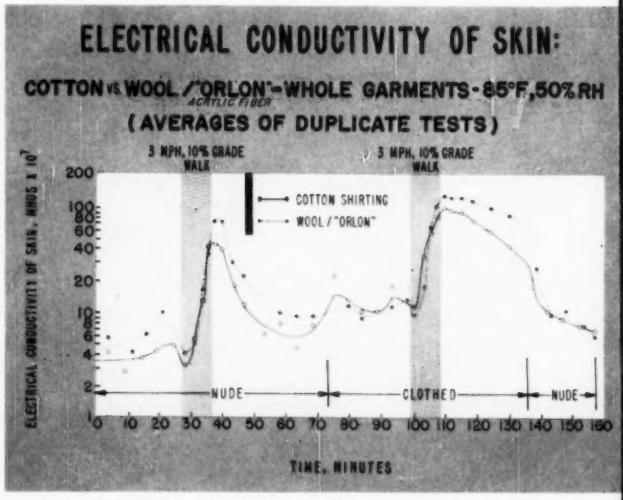


FIG. 9

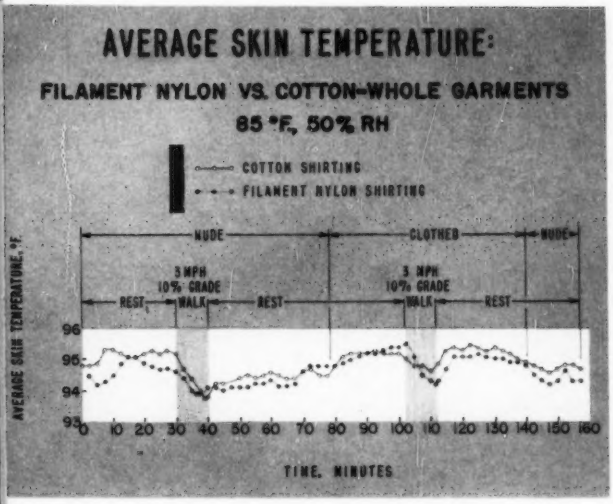


FIG. 10

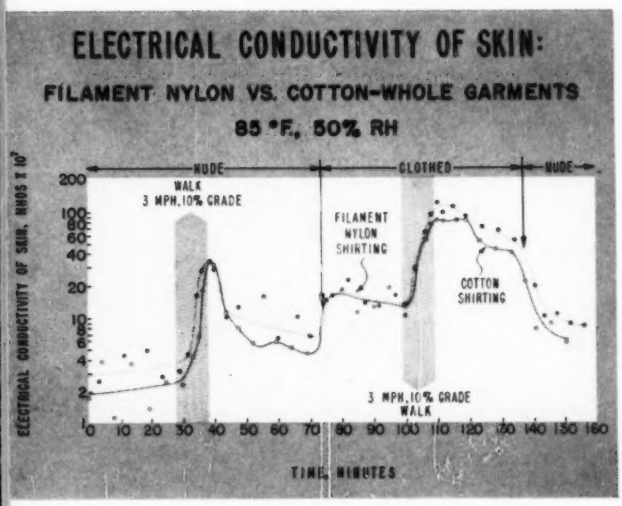


FIG. 11

To demonstrate with human subjects the effect of increased air movement, the fabric tests were repeated. Figure 12 compares results of tests for wool/*Orlon* acrylic fiber, nylon, and cotton—first, at the usual 0.3 m.p.h. air movement and then at 3.5 m.p.h. wind speed. Through the period of lower air movement, the wool/*Orlon* again produced the highest average skin temperature. However, when the subject was exposed to a 3.5 m.p.h. air velocity generated by the 24-in. fan, the average skin temperatures produced by wearing any one of the three fabrics fell to the same general level; and by comparing the maximum skin temperatures attained in each of the two periods of different wind speed, it was observed that the greatest lowering of skin temperature occurred in wearing the more loosely woven wool/*Orlon*. Thus, by changing one variable, the experimental data were brought in the direction predicted by the physical study. This again emphasizes the importance of defining the environmental conditions to which the comfort evaluations apply. Similarly, control of the air gap between fabric and skin may bring the two studies into complete agreement.

The number of tests is not yet sufficient to conclude firmly that statistically significant physiological differences are produced by the conventional fabrics studied thus far. However, it is believed that the measured changes at the body surface attributed to different fabrics cannot be expected to be as large as the physiological variations associated with changes in test environment or in proceeding from the nude to the clothed state.

Comparative Sweat Costs

Another possible criterion of comfort is provided by measuring the relative amount of weight loss due to perspiration while wearing garments of different fabrics. This factor is known as "sweat cost"; and the fabric causing the greatest sweat cost, all other things being equal, puts the greatest stress on the body ([4], pp. 338–51). Differences in sweat cost which could be attributed to different fabrics have been explored in both short- and long-term tests of 1 hr. and 7 hrs. duration.

Typical of the short-term tests were comparisons of three fabrics: a filament nylon; a fairly heavy cotton denim; and a spun nylon denim, made to duplicate the fabric geometry of the cotton material (fabrics *4*, *5*, and *6*, Table I). The comparisons were made with subjects wearing the usual loose-fitting coverall garments in the test room conditioned

to 95°F and 50% R.H. Figure 13 shows the cumulative weight loss through the course of an experimental routine performed by three individuals, each of whom tested all of the garments. As indicated by the clear and shaded areas, the subject worked at the rate of 360 kg.-m./min. by pedaling the bicycle ergometer between periods of rest, first in the nude and then clothed in the test garment. During a third and final period the subject stood in a 9 m.p.h. wind generated by the fan. Arrows indicate the times at which the garments were put on and removed, and the points making up the individual curves represent cumulative weight loss as determined by weighings taken at given time intervals.

At first glance the relative positions of the curves suggest that sweat cost during the intermediate part of the test was the least in cotton. However, this is only an apparent advantage for cotton since the body perspired essentially the same amount in all of the fabrics, as shown by the equivalence of total weight loss which was determined by weighing the subjects nude at the end of the experiment. Only the difference between initial and final weighings in the nude can represent actual sweat cost. Since this weight differential is given by the final point of each curve, the sweat costs in the three garments differed only by 30 g. in a total weight loss of more than 400 g. The curve for cotton does not coincide with the nylon curves due to the greater capacity of the cotton garment for water absorption. Most of the water vapor entering the two nylon garments simply went through the fabric and was dissipated to the environment, whereas in the case of cotton, a higher percentage of the perspiration was absorbed in the fabric. The three intermediate weighings were made with the garment on, and the moisture retained by the cotton fabric accounts for the apparently lower weight loss.

A table of the average rate of weight loss (Figure 13) shows again the close similarity of all three fabrics in their effect on sweat cost. The table of the average weight increase of the three garments confirmed the greater moisture absorption of the cotton denim even when the garments were almost dry.

Sweat costs associated with the filament nylon and cotton shirtings (fabrics *2* and *3*, Table I) were compared in duplicate 7-hr. tests. Each of two subjects tested garments of both fabrics in an environment of 90°F and 55% R.H. During each of seven time-cycles the subjects walked for 10 min. at 3 m.p.h. on the treadmill inclined to 10% grade. The exercise

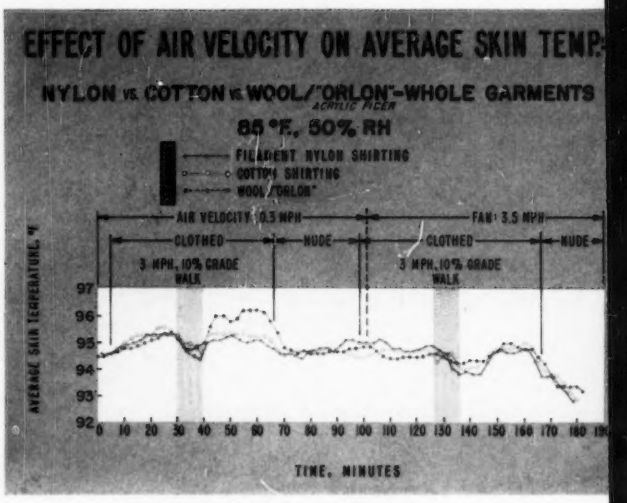


FIG. 12

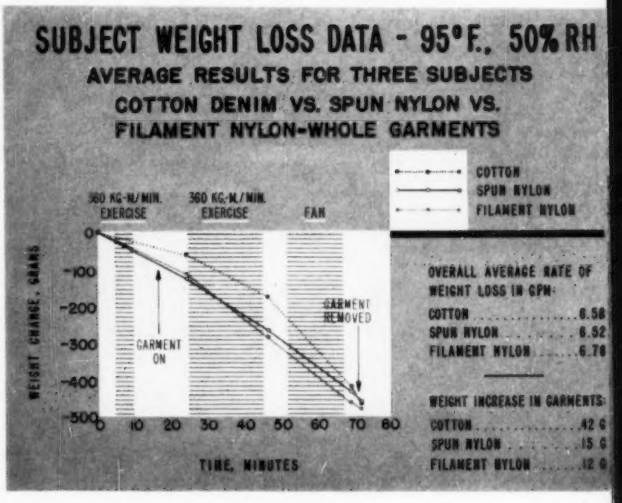


FIG. 13

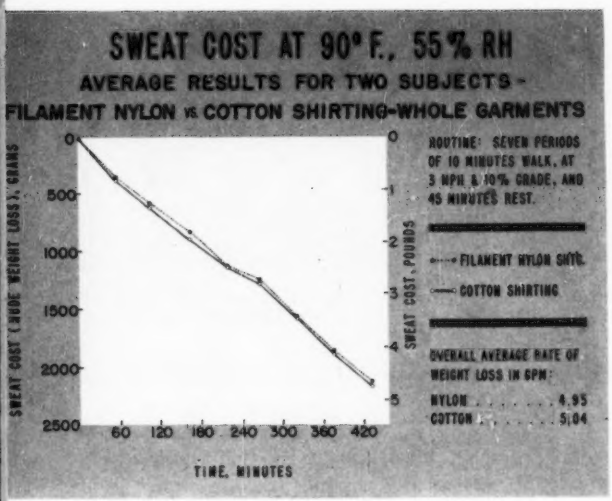

SWEAT COST AT 90° F., 55% RH
AVERAGE RESULTS FOR TWO SUBJECTS -
FILAMENT NYLON vs COTTON SHIRTING-WHOLE GARMENTS
SWEAT COST (NUDE WEIGHT LOSS), GRAMS
SWEAT COST, POUNDS
TIME, MINUTES
ROUTINE: SEVEN PERIODS OF 10 MINUTES WALK, AT 3 MPH & 10% GRADE, AND 45 MINUTES REST.
FILAMENT NYLON SHTG.
COTTON SHIRTING
OVERALL AVERAGE RATE OF WEIGHT LOSS IN GPH:
NYLON 4.95
COTTON 5.04

FIG. 14

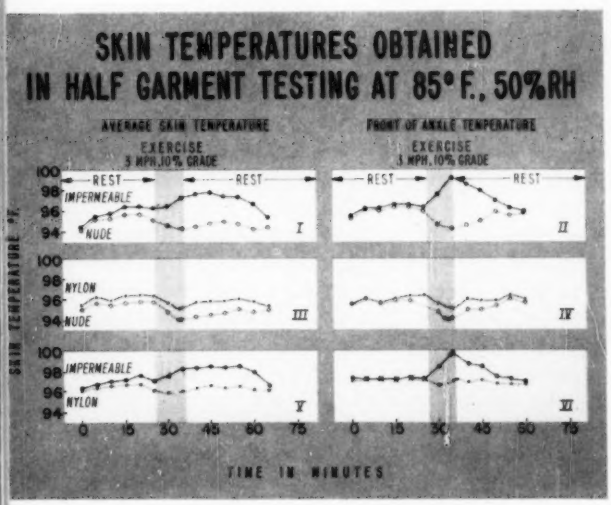


FIG. 15

was followed by 45 min. of rest, after which the coverall test garment was removed only for the time required to determine the subject's weight in the nude. The garment was put on again; and before another period of exercise and rest, the weight lost during the previous cycle was replaced exactly by drinking an equivalent amount of water. For each of the fabrics the average of the cumulative sweat costs of the two subjects is shown as a time variable in Figure 14. The curves are quite parallel and nearly superimposable, demonstrating that lightweight, similarly constructed fabrics of nylon and cotton do not differ significantly in their effect on the rate at which the body perspires or on total sweat cost. The slight change in the slope of the curves halfway through the experiment was due to an interruption for lunch. At no time during the 7-hr. period did the subjects leave the test environment. In order to insure that the test was not invalidated by removing the garments before each weight determination, the original conclusion was verified by tests in which the subject remained clothed throughout the experiment.

Half-Garment Testing

In addition to the use of complete coverall garments in the experimental procedures described thus far, other methods of test were based on the wearing of half-garments. These half-garments were prepared by simply splitting the whole coverall into a left and a right half and providing a zipper in place of the original seam. The two half-garments could then be joined directly, or each half could be zippered to a center strap of cotton fabric worn tightly against the stomach and back, thereby restricting movement of the air between the garment and skin from one side of the body to the other. It will be shown that skin temperature differentials were established between the two sides of the body by providing each with a different clothing environment; and, with reference to the magnitude of the temperature differentials, the procedure was applied to the comparison of fabrics. As shown in Figure 2, half-garments of two different fabrics could be worn for simultaneous comparison, with the advantages that day-to-day physiological variations are eliminated and fewer tests should be required for adequate fabric evaluations.

Early experiments in half-garment testing defined the extreme limits of the average skin temperature differential established when the two halves of the body were functioning at different levels of heat

stress. This was done by leaving one side of the body nude and clothing the other in a half-garment of rubberized nylon material. The fabric was impermeable; and under warm environmental conditions imposed a rigorous heat stress on one side of the body by severe limitation of evaporative cooling.

Half-garment testing was conducted in an environment of 85°F and 50% R.H., and exercise consisted in walking at 3 m.p.h. on the treadmill elevated to 10% grade. As usual, the routine of rest, exercise, and rest was performed twice, first in the nude and then wearing the half-garment. Skin temperatures recorded during the clothed part of the test are shown in Figure 15. The two curves of graph *I* show the average surface temperatures for both sides of the body, the upper curve representing the temperature behavior of the skin covered by the impermeable fabric and the lower curve following the temperature variations of the exposed surface. At the close of the exercise period the average temperatures for the two body halves differed by 3°F, and this differential was maintained for some time during the final rest period.

Graph *II* shows the contribution to the average made by the individual surface temperatures measured just in front of the ankles. The greatest temperature difference between any two of the symmetrically paired thermocouple locations was found at this foot position, where a maximum differential of 5°F occurred at the end of exercise. This magnification of the trend shown by average skin temperature is not unexpected since physiological research [3] has shown that the surface areas of the lower extremities reflect to the highest degree increasing or decreasing peripheral blood circulation by which the skin is caused to increase or decrease the rate of body heat loss. The extremities, particularly the feet, are therefore sensitive indicators of temperature changes occurring at the body surface.

It is clear from the above experiment that skin temperatures can reflect different degrees of stress applied simultaneously to opposite sides of the body and that the differences were most strikingly evident at the foot.

The remaining graphs shown in Figure 15 represent variations of average and foot temperatures when a half-garment of nylon (fabric *3*, Table I) was worn alone (graphs *III* and *IV*) and together with the impermeable half-garment (graphs *V* and *VI*). In each of the tests the nylon half-garment has replaced one of the conditions imposed on half the body

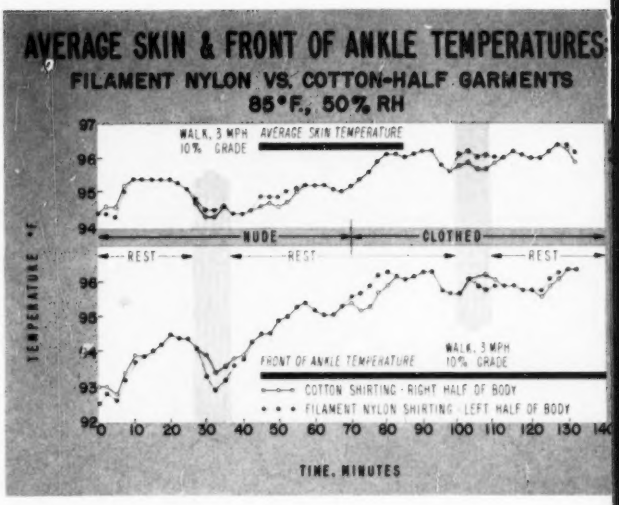


FIG. 16

in the original comparison of the completely sealed and nude surfaces. Assuming that in a warm environment greater discomfort is experienced as skin temperatures increase, the nylon appears to be more comfortable than the impermeable fabric and the temperature curves representing the two sides of the body lie closer together (graphs *III* and *IV*). The same is true in wearing the two half-garments simultaneously (graphs *V* and *VI*) since any garment is less comfortable than the nude in this environment. It was noted again that the foot temperatures (graph *VI*) show a larger temperature differential than do the average temperatures (graph *V*).

If any half-garment is more comfortable than the nylon, the curves of graph *III* should approach still more closely and the curves shown in graph *V* should become more widely separated as in the original comparison of extremes (graph *I*). This analysis compares the test fabric against two extreme standards—the exposed skin surface and the sealed surface; and conclusions depend on the temperature differentials established thereby. Preliminary applications of the technique using half-garments of the nylon, cotton, and wool/*Orlon* acrylic fiber have shown the nylon and cotton shirtings to be essentially the same with respect to their influence on skin temperature and the wool/*Orlon* to be relatively warmer, as was shown in some of the whole-garment testing carried out under the same environmental conditions.

Although use of the impermeable fabric establishes relatively large temperature differentials between the

two sides of the body, comparisons have been made directly by wearing half-garments of the test fabrics simultaneously. This was done by testing a subject with the cotton on one side and the nylon on the other (fabrics *2* and *3*, Table I). Average skin temperatures and foot temperatures are shown in Figure 16. Throughout the test no significant temperature differences were evident between the two halves of the body even at the foot locations. This variation of half-garment testing again shows that the nylon and cotton shirting materials are very similar in their effect on body surface temperature.

Subjective Opinion of Comfort

Essential to a comprehensive study of clothing comfort is the evaluation of subjective opinion solicited from the individual wearing a test fabric, and, furthermore, it is necessary that this opinion correlate with conclusions based on the objective data. Procedures to obtain only subjective opinion were similar in routine to those designed for measuring the physiological responses to different fabrics. However, measuring devices necessary to the latter technique were not used. To evaluate the test subjects' impressions of comfort and wetness, these factors were expressed by numerical ratings at frequent intervals during the test—for example: 0 meant comfortable; 1, slightly uncomfortable; 2, moderately uncomfortable; and 3, very uncomfortable. Numbers were also used to describe the sensations of being dry, slightly wet, moderately wet, or dripping wet. In addition to these ratings, each set of comparative tests was followed by a carefully designed interview in which the subject was asked a number of standard questions. There was also opportunity for him to volunteer any further information not covered by specific questions.

In early subjective tests, different individuals arranged the two or three fabrics being compared in different orders of preference. This suggests the possibility that people will fall into preference classes depending on the types of apparel to which they have become accustomed through experience and for which definite likes or dislikes have developed. In certain cases the opinions obtained during the interview and the ratings given during the test were not in agreement. No satisfactory explanation for the discrepancies is immediately apparent, but new tests based on the half-garment method are being designed to eliminate reliance on memory for comparative subjective evaluations.

TABLE II. SUBJECTIVE TEST OF SHIRTS AT −6°F

Shirt	Cold ratings* Subject *A*	Subject *B*	Subject *C*	Subject *D*	Averages
Spun nylon	1	0.5	0	1	0.63
Heavy, fuzzy cotton	1	1	0.5	1.5	1.00
Light cotton	1.5	2−	1.5	2	1.75−
Filament *Dacron* polyester fiber	2	2+	1	2	1.75+
Filament nylon	3	3	2.5	2.5	2.75

* Subjective thermal impressions: 0 = comfortable; 1 = slightly cool; 2 = cool; 3 = cold.

It is difficult for an individual to exclude the elements of fabric color, appearance, hand, and related factors which affect his opinions of comfort. In an attempt to remove these distracting influences, subjective tests were run with individuals blindfolded and wearing gloves so that they could neither see nor handle the fabrics. Opinion was then presumably based only on the sensations stimulated by wearing the garment—*e.g.*, warmth, dryness, surface characteristics. These refinements were employed in twenty-four tests on eight individuals, but no appreciable improvement in the consistency of subjective ratings was achieved. All of these evaluations were obtained in an atmosphere which was uncomfortably hot, particularly during exercise, and it may be that more reliable impressions will be forthcoming when the tests are made under less severe conditions.

Still other contributions to comfort are attributed to the tactile qualities of clothing. To demonstrate their effect, four individuals evaluated five commercial shirts of different surface texture, including materials of filament nylon, spun nylon, heavy fuzzy cotton, light cotton, and filament *Dacron* polyester fiber. Subjective impressions were obtained as the test subjects stepped into a cold locker at −6°F for a period of from 1 to 2 min. Their ratings of the shirts are shown in Table II. The numbers refer to a comfort scale ranging from 0 (comfortable) to 3 (cold). There was remarkably good agreement among the four individual evaluations, and the average ratings place the shirts in the following order from warmest to coldest: spun nylon, heavy fuzzy cotton, light cotton, filament *Dacron*, and filament nylon. At a glance it was evident that the spun nylon was by far the fuzziest of the materials, and the filament nylon the smoothest and flattest. The marked chill sensations experienced in wearing the continuous filament

nylon were undoubtedly associated with the intimate skin contact made by the smooth, flat surface. As a result, more heat was transferred from the skin to the shirt than would flow if the garment had been standing away from the body surface on the ends of staple filaments as in the case of the spun nylon. Here were two items of apparel made from the same nylon polymer, yet rated at extreme ends of a comfort scale; this was believed to be due to the characteristic difference between staple and continuous filament yarn. These shirt tests indicate again the significant influence of fabric construction on the human sensations which define a state of comfort or discomfort. Closely related to this phase of the comfort study are ratings of the "chilling effect" or "clammy feel" of moist fabrics [2].

It is also possible that tactile sensations are important but more obscure to comfort evaluations in a hot environment and might be manifested in, for example, differences in the tendency of garments to cling to a body surface wet with perspiration. The fabrics tested in the hot environments certainly differed in surface texture, leaving the observed inconsistencies to be explained perhaps on the supposition that individuals differ in their concept of the most comfortable surface texture.

Summary

Certain physiological factors such as skin temperature, degree of skin wetness, rate of sweating, total sweat cost, and heart rate were measured as presently accepted criteria of human comfort. These parameters were utilized in the evaluation of several textile fabrics chosen for test on the basis that such measurements would confirm expected differences in comfort. In a warm humid environment differences between fabrics, as indicated by the measured physiological responses, were small and in some cases nonexistent. Although the amount of data is still rather limited, it will be analyzed further to determine whether or not a sufficient number of experiments have been performed to establish firmly that the observed differences in skin temperature are statistically significant.

Quite apart from the accumulation of objective data, subjective opinion was solicited for the evaluation of fabric comfort. Although impressions of clothing comfort in a hot, humid atmosphere were inconsistent, meaningful comfort ratings were obtained in a cold environment with good agreement among the test subjects.

Thus far the experiments have indicated that comfort largely depends upon the geometry of fabric construction and the manner in which the fabric is worn on the body. This general conclusion was in accord with information obtained from laboratory equipment designed to evaluate the thermal properties of fabrics independently of the tests on human subjects [1].

With further testing, improved correlation between the human subject and physical studies is anticipated; and, ultimately, the observed physiological and psychological responses should serve to calibrate laboratory instrumentation designed to predict the comfort value of a given textile fabric for use in any given environment.

Acknowledgment

The authors wish to acknowledge the contributions made to the physiological part of the work by Lucien Brouha, Medical Division, and Paul E. Smith, Jr., Haskell Laboratory of Industrial Toxicology, E. I. du Pont de Nemours and Company, Inc. Certain of the purely physiological data will be published by Dr. Brouha at a later date.

We are also grateful for the suggestions and counsel of L. P. Herrington, School of Medicine, Yale University; and of R. M. Hoffman and L. G. Ray, Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc.

The special modification for the Brown recording instrument was developed by C. G. Dell and L. P. Haner, Engineering Research Laboratory, E. I. du Pont de Nemours and Company, Inc.

The thermocouple and electrical conductivity units were constructed by H. L. Rash, T. S. Sitewicz, and J. F. Ireland, Chemical Department, E. I. du Pont de Nemours and Company, Inc.

The authors are indebted to technical personnel at the DuPont Experimental Station who volunteered as subjects for the testing program.

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* (*Manuscript received October 17, 1952.*)

Improvement of Luster of Cotton

Part II: Decrystallizing and Mercerizing—Influence on Luster*

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Abstract

Anhydrous ethylamine and solutions of sodium hydroxide both affect the luster of cotton yarns in the same direction as well as having similar effects on properties which indicate decrease of crystallinity, or increase of accessibility of the cellulose. However, the extent of the effect is less for ethylamine, under the conditions examined, with one exception. When the cotton yarn is held at nearly constant length by wrapping on plates, with minimum possibility of mechanical action, the ethylamine treatment has more effect on moisture sorption, though less on luster, than the relatively low degree of mercerization obtained on plates.

Tension or control of length is required to produce luster; treatment by either ethylamine or sodium hydroxide solution without tension decreases the luster. Luster is increased more by mercerizing after the ethylamine treatment than by the ethylamine treatment after mercerizing, holding the yarn at original length. The stretching of the yarn, which is made possible by a swelling treatment, and the improvement of fiber roundness are more important for high luster than the degree of change of crystallinity of the cellulose. Thus, measures of accessibility, such as "barium number," do not indicate changes in luster primarily, but only indirectly and in limited ranges in which there is definite stretching of the yarn and with the important condition that final yarn length is constant in the group being compared. In these special cases the accessibility measure can indicate the degree of action of the swelling agent and can parallel the effect on luster.

SINCE it has been shown by Segal, Nelson, and Conrad [4] that treatment of cotton by anhydrous ethylamine has a great effect in decreasing the crystallinity of cotton, and has a strong swelling effect, it is of interest to compare this type of swelling treatment with the more familiar mercerization in their effects on luster.

It is well known that the effect of mercerizing on luster depends not only on the swelling of the cotton by the sodium hydroxide solution, and the permanent improvement in roundness of fiber which results, but also on the tension in the cotton, or the length to which the yarns are held or stretched. Hence, the effect of the ethylamine treatment has been studied both without tension, allowing the yarn to shrink freely, and with tension, by holding the yarn at original length.

This work permits a closer look at the relations between measures of crystallinity, or of accessibility, such as regain or barium number, and the effect of mercerization on luster. Barium number was originally proposed as a measure of the extent of reaction in mercerizing [1a], but more recently it has been suggested that "generally the fabrics with high barium numbers also show the best strength, luster and wear resistance" [1d]. The present tests indicate limitations on this generalization with regard to luster.

Method

The control of tension, or, more correctly, length, in the ethylamine treatments was accomplished by winding the yarn on stainless-steel plates, in such form that these windings could be used for measurement of luster. The difficulties arising from the low boiling point (16.6°C) of ethylamine were reduced by cooling all materials to 0°C and using a stainless-steel pressure cooker for the treating bath. The cotton on the plates was dried at 105°C and cooled in a

* A report of work done under contract with the U. S. Dept. of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry. This paper is based on material presented at the Conference on the Chemical Finishing of Cotton held by the National Cotton Council in Washington, D. C., Sept. 25, 1952.

Part I appeared in the July, 1951, issue of TEXTILE RESEARCH JOURNAL, p. 469.

desiccator before treatment. Treatment with ethylamine was for 4 hrs. at 0°C, after which the skeins or plates were rinsed in chloroform and let dry in air at room conditions.

Controls which were mercerized on similar stainless-steel plates were neutralized and washed on the plates and measured for luster after drying. It was found that the tightly wound yarn was not washed completely on the plates, so the yarn was removed, washed in skein form, and measured again for luster. All measurements of moisture sorption were made on yarn which had been washed in skein form.

All measurements of luster are in terms of the contrast ratio, in which higher contrast ratio corresponds to higher luster. Contrast ratio is defined as follows:

$$C_R = \frac{\text{reflectance for 45° view, 45° illumination}}{\text{reflectance for 45° view, 0° illumination}}.$$

In this, all angles are measured from the normal—that is, the line at right angles to the general surface. Thus, luster is measured in terms of the amount of light concentrated in the direction in which a mirror would reflect, in comparison to the light scattered at a representative non-mirror angle direction. The optical methods have been described elsewhere [2, 3].

Mercerizations were with 23% sodium hydroxide solution containing a mercerizing wetting agent and were carried out at room temperature. This concentration of caustic has been found to be near the center of the optimum concentration range for luster, under the laboratory conditions of mechanical handling and temperature. In mercerizing skeins, these were rinsed, neutralized, and rinsed again on a mercerizing frame on which the skein could be rotated in order to secure uniform treatment. The length was held constant through these skein processings (except in the series described in the discussion and Figure 2) but the skeins were allowed to dry slack.

Length of skein was measured under a uniform tension equal to 136 g. load times the number of turns in the skein divided by the equivalent singles cotton count.

All of the yarn used in these trials was from ten cones of one lot of commercially spun yarn of Acala 4–42 cotton, 36/2 cotton count, with mercerizing twist. Except for the results given in Table II, which are for individual plates, each measurement is the average for from 2 to 5 skeins, randomized from the supply. Kiering was done in the laboratory by heating skeins for 4 hrs. at 15 lbs. pressure in a solution containing 15 g. sodium hydroxide, 2.5 g. sodium carbonate, 2.5 g. sodium metasilicate, 3 ml. pine oil, and 3 ml. oleic acid in 1000 ml. of water.

Results

Treatment without Tension

The results of trials of treatment with ethylamine without tension are shown in Table I. Treatment

TABLE I. ETHYLAMINE TREATMENT OF COTTON WITHOUT TENSION

Series	Treatment	Barium number	Moisture regain* (%)	Final length† (%)	Luster (contrast ratio)
	Control: raw yarn	100		100	1.70
A	Kier, water wash		5.3	96	1.54
	Kier, chloroform wash		5.4	96	1.53
	Kier, ethylamine slack		6.1	86	1.41
B	Kier, ethylamine slack	134		89	1.62
	Kier, ethylamine slack, then mercerize at original length	161			2.50
	Kier, ethylamine slack, then mercerize at 103% of original length	160			2.62
C	Raw yarn, ethylamine slack			88	1.53
D	Kier, ethylamine slack		8.3	86	1.54
	Kier only		6.9	96	1.61
	Kier, mercerize slack		9.6	84	1.48
	Kier, mercerize at original length		8.4	98	2.38
	Kier, ethylamine slack, then mercerize at original length		8.9	98	2.56
	Kier, ethylamine slack, then mercerize slack		9.9	86	1.50
	Kier, mercerize slack, then ethylamine slack		9.4	82	1.53
	Kier, mercerize at original length, then ethylamine slack		8.6	91	1.96

* Moisture was determined as regain by conditioning at 65% R.H. and 21°C: for series *A*, after drying at 105°C for 4 hrs.; for series *D*, after drying at 110°C for 2 hrs.

† Final length is given as percent of original raw yarn length.

with ethylamine shrinks the skeins to between 86% and 89% of the original length, which is somewhat less shrinkage than is obtained by mercerization without tension (77%–84%). The luster of the cotton treated with ethylamine in the absence of tension is low, and varies from trial to trial in the same low range as the luster of yarn which is mercerized while slack. None of the treatments without tension, including kiering, increases the luster above that of the raw yarn.

Series *B* and *D* show that treatment with ethylamine while the yarn is slack causes it to reach higher levels of luster after mercerization than are reached by similar mercerization conditions with kiered or grey yarn. Part of this effect may come from the mechanical action of stretching the yarn which had shrunk freely in ethylamine. However, yarns held at original length while being treated with ethylamine also give increased luster when subsequently mercerized, as shown in Table II. However, the luster secured by mercerization after ethylamine treatment can be exceeded by that which can be produced by stretch, or by repeated slacking and stretching, in regular mercerizing with caustic, as shown by the examples given in Figure 1, which go as high as 2.73 in contrast ratio.

Measurements of moisture regain in series *A* and *D* show that the crystallinity of the cotton is reduced by ethylamine treatment, as indicated by greater accessibility of the cellulose, with more sites for the sorption of water. However, mercerizing by sodium hydroxide solution, especially when the yarn is slack, causes larger increases in regain, as shown in Figure 2. Mercerization after treatment with ethylamine (series *D*) markedly increases the moisture absorption.

Series *D* also shows that if the yarn is first mercerized slack and then treated with ethylamine while slack, the results are not very different from mercerizing slack by itself, or from treating first with ethylamine and then mercerizing, both slack. How-

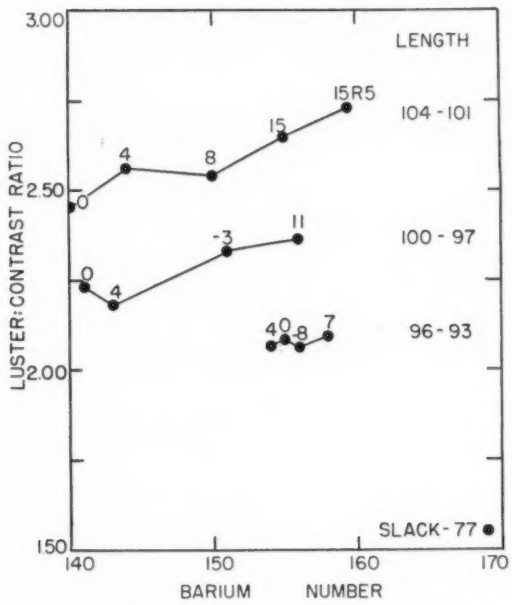

FIG. 1. *Relation between luster and accessibility or decrystallization of cotton cellulose, which is measured by the barium number, for different conditions of stretch and mechanical action on the yarns during mercerizing. The numbers under "length" indicate the final length during mercerizing and after drying, respectively, for the several groups of points. The numbers close to the points indicate the stretch (or negative slacking) while in caustic, expressed as percent of original length. The combination 15 R5 indicates that this 15% stretch was repeated 5 times, with slacking off between.*

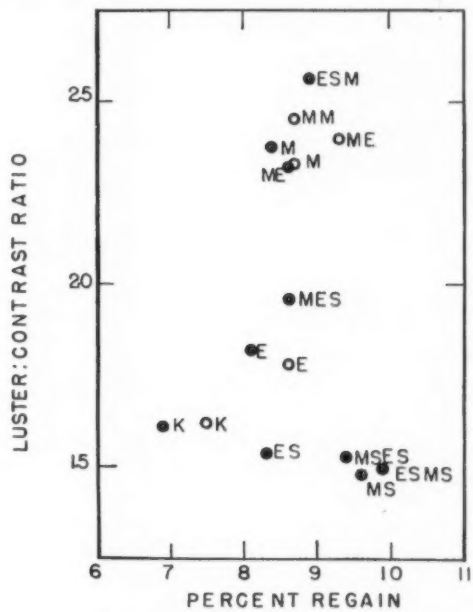

FIG. 2. *Relation between luster and the degree of accessibility or decrystallization, as indicated by moisture regain. Two sets of results are shown, series C by open circles and series D by solid circles. The letters close to the points indicate the treatment and order of treatment:* K = *kiered only (all the yarns were kiered);* E = *treated with ethylamine under tension at kiered length;* ES = *ethylamine treatment slack;* M = *mercerization under tension at original length;* MS = *mercerization slack. The order of symbols indicates order of treatment; thus,* ESM *means ethylamine treatment, slack, followed by mercerization with tension.*

TABLE II. EFFECTS OF ETHYLAMINE TREATMENT, UNDER TENSION, ON KIERED YARN

Plate	Treatment	Luster (contrast ratio) On plates Original	Luster (contrast ratio) On plates Treated	Luster (contrast ratio) Removed Washed	Moisture regain* (%)	Barium number
A	Control, washings only	1.57	1.62	—	6.76	—
H		1.54	1.61	—	6.81	—
C	Mercerize only	1.53	2.07	1.81	8.20	133
E		1.60	2.18	1.95	8.24	137
B	Ethylamine only	1.60	1.86	1.70	8.40	133
D		1.53	1.78	—	—	—
F		1.54	1.77	—	—	—
G		1.57	1.80	—	—	—
D	Ethylamine, then mercerize at 100% natural length	—	2.44	2.14	8.71	148
F		—	2.32	2.07	8.92	151
G		—	2.39	1.95	8.91	148

* Equilibrium with 21°C and 65% R.H. atmosphere, for yarn washed after removal from plates. This set of yarns was dried after conditioning rather than before.

ever, treatment with ethylamine without tension after mercerizing with tension has only a slight effect on regain, but does produce shrinkage and decrease of luster. The shrinkage, to 91%, is less than that of yarn which has not been mercerized under tension, and the luster (1.96) is above that of the raw yarn, or above that of yarn treated with ethylamine under tension, as indicated in Figure 2.

Measurement of barium number [1b] in series *B* shows that this measure of accessibility or decrystallizing is also increased by ethylamine treatment, but is increased further by subsequent mercerization.

Treatment with Tension

The results of trials of treatment with ethylamine, holding the cotton at original length, are shown in Tables II and III.

Table II shows that ethylamine treatment with tension does increase the luster, but not as much as does mercerization under similar conditions. The ethylamine treatment reduces the crystallinity more than mercerizing under these particular conditions, as shown by the higher moisture regain. However, barium number, which is often used as an indicator of mercerizing, is relatively low for mercerized yarn, and shows no difference between mercerization and ethylamine treatments on plates. The barium number appears to be the same for ethylamine treatments with and without tension.

That the ethylamine treatment does not go so far as mercerizing does in producing luster is also shown in Table II by the increase of luster obtained by mercerizing after treatment with ethylamine. This combined treatment also increases both moisture regain and barium number, indicating further reduction in crystallinity.

The comparisons of treatments under tension in Tables II and III differ, in that all the ethylamine treatments and the mercerizings in Table II were on plates, while the mercerizings in Table III were in skein form on the roller frame, in which the skein could be rotated and more effective mercerization secured.

Table III shows that yarn which has been mercerized under tension is not greatly, or at least consistently, affected as to luster by a subsequent treatment with ethylamine, also with tension, although the ethylamine increases the regain above that after the original mercerizing. This adds to the indications

TABLE III. KIERED YARN, MERCERIZED OR TREATED WITH ETHYLAMINE UNDER TENSION

Treatment	Luster (contrast ratio) *C*	Luster (contrast ratio) *D*	Moisture regain* (%) *C*	Moisture regain* (%) *D*
Kier	1.62	1.61	7.50	6.9
Mercerize at original length (skeins)	2.33	2.38	8.7	8.4
Mercerize twice at original length	2.45		8.7	
Ethylamine	1.78	1.82	8.6	8.1
Mercerize at original length, then ethylamine	2.40	2.32	9.3	8.6

* Moisture was determined as regain by conditioning at 65% R.H. and 21°C after drying at 110°C for 2 hrs.

that ethylamine has greater effect on the crystallinity than on the luster.

The results of both series in Table III are plotted in Figure 2, along with the portion of series *D* involving slack skein treatments, for which other data are given in Table I. This graph shows the general consistency of the two series. The moisture regains in the different series give somewhat different results. The regains within each series are comparable, because all specimens in each individual series were treated similarly, but the general level of moisture content in the various series is different, owing to differences in extent of drying prior to conditioning and to possible day-to-day differences in the conditioning room, among possible causes.

Discussion

One of the important differences between the effects of ethylamine treatment and of mercerizing with sodium hydroxide is that after the ethylamine treatment, the portion of the cellulose which remains crystalline is still cellulose *I*, or native cellulose, in crystal structure, while after sodium hydroxide mercerization, the cellulose is more or less completely converted to hydrate cellulose, cellulose *II* [4]. Conrad and coworkers find that this kind of ethylamine treatment does not produce hydrate cellulose. These differences of crystal structure may affect the sorption of water or of barium hydroxide, so that these measures of accessibility do not have the same significance with regard to degree of crystallinity for the two kinds of treatments. This may account for the fact that on the whole these measurements show greater changes in accessibility measures after mercerization, although Segal, Nelson, and Conrad [4] found that larger changes in crystallinity are caused by ethylamine treatment.

The results are more conclusive in showing that the decrystallizing effects and the luster-producing effects of treatments by strong swelling agents such as anhydrous ethylamine and sodium hydroxide are independent. Both are related to swelling, but the luster effects also involve stretching of the yarns and thus, probably, improved arrangement of the fibers.

This independence is shown in Figure 2, in which large changes in regain produced by slack yarn treatments involving mercerizing cause only a small change in luster, in comparison with slack treatment with ethylamine, while large differences in luster with only small differences in regain are caused by treatments with tension.

This independence is also illustrated in Figure 1, which shows the relation between luster, length, degree of mechanical action on the yarns during mercerizing, and decrystallization, as indicated by increasing barium number. At the same barium number, wide variations in luster can be had, depending on the conditions of mercerizing. Individual points of three groups of mercerizing conditions are connected by lines; the fourth condition, mercerizing completely slack, is represented by an isolated point at low luster, but at the highest barium number.

Each group of mercerizing conditions has as its common element the same final length on the mercerizing frame. The members of each group were wet by caustic at varying initial lengths, and were stretched or slacked to varying degrees to reach the final length characteristic of their group. The final lengths on the mercerizing frame were 104%, 100%, and 96% of original length, but the corresponding lengths after drying were 101%, 97%, and 93%, to which one can compare the final length, 77%, of the skeins mercerized completely slack. The number close to each symbol in the groups indicates the percent change of length between wetting with caustic and final condition in caustic. This final condition—*i.e.*, 104%—was maintained through rinsing, neutralizing, and final washing.

The highest group with respect to luster, that ending at the highest stretch, 104% of the original length, covers the same span of barium number as the groups of lower luster and lower stretch. Within the highest group itself, there is an upward trend of luster and barium number, but this is in turn connected with variations in the amount of mechanical action on the yarns—that is to say, on the extent of exposure to the action of the mercerizing solution. The groups of lower final length and lower luster are not as consistent in showing a relation between mechanical action and luster, or mechanical action and barium number. The skeins mercerized completely slack shrank to 77% of original length, and had lower luster than the grey yarn (contrast ratio 1.55, as compared with 1.78) but the highest barium number of all.

The results within the uppermost group indicate the effect of increased action of the swelling agent and of mechanical action, and probably are accompanied by improved fiber shape, since the fiber arrangement, which is influenced by final length, must

be almost the same within this group; the results in Figure 1 as a whole indicate that swelling and decrystallizing are important to luster not merely by changing fiber shape, or changing internal crystallinity, but also by giving an opportunity to stretch the yarns, so that the resulting luster depends also upon the degree to which this opportunity to stretch is utilized.*

There are at least four possibilities for the mechanism by which stretching acts to increase luster: (*1*) improved arrangement of the fibers with respect to the yarn direction; (*2*) improved parallelization of neighboring fibers; (*3*) improved smoothness and roundness of fiber surface; (*4*) improved orientation of crystallites within the fibers, even with reduction in over-all crystallinity.

The present work does not bear directly on these four possibilities, although it shows that substantial decreases in crystallinity can be accompanied by substantial increases in luster, indicating that external surface or geometrical factors are probably more important to luster in cotton than differences of internal structure, unless the effect of improved orientation of remaining crystallites and improved orientation in the amorphous region is very large indeed.

* This is in accord with the work of Edelstein [1c] in which barium number is proposed to "measure the completeness of the reaction which has taken place between the mercerizing caustic and the material," but in which it is also pointed out [1a] that "barium activity numbers . . . were found to be unaffected by the amount of tension during mercerization," while "for any particular caustic solution the greater the tension put on the yarn, the greater was the luster of the finished yarn."

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(*Manuscript received October 30, 1952.*)

The Fractionation of Cellulose

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Abstract

Studies of molecular weight heterogeneity have been carried out on various celluloses, both before and after exposure to the degradative effect of ultraviolet radiation. Fractionation was carried out on the nitrate derivatives of the samples studied. The data show that significant changes have taken place in the molecular weight distribution patterns of the degraded celluloses.

Introduction

It is well known that cellulose is not a homogeneous material with respect to molecular weight or chain length. Moreover, the physical and mechanical properties of a given cellulosic product are dependent upon the character of its molecular weight distribution as well as upon its average molecular weight.

Many approaches to the fractionation problem have been presented in the literature. Kumichel [10], Straus and Levy [22], and Battista and Sisson [2], among others, have fractionated cellulose in various solvent systems. Fractionations of cellulose derivatives are reported by many workers, including Sookne, Rutherford, Mark, and Harris [20], Mitchell [13], Davis [5], Herrent and Govaerts [6], Coppick, Battista, and Lytton [4], and Heuser and Jörgensen [7].

The theoretical aspects of fractional separation of heteromolecular high polymers have been extensively

treated by Schulz and Nordt [19], Morey and Tamblyn [15], and Morey [14]. Beall [3] has investigated the mathematical statistics of the molecular weight distributions obtained in fractionating cellulose, and has proposed a binomial distribution as characteristic of this material.

The present work has been carried out by fractionation of nitrate derivatives of the various celluloses investigated by precipitation from an acetone solution using distilled water as precipitant. We have found that precipitation separation of the nitrate derivative of the sample gives consistent results in our work, and lends itself to satisfactory interpretation with a degree of work that is consistent with practical considerations. Fractionations have been carried out on pulped cotton cellulose and on tire cord viscose rayon. Changes in molecular weight distribution with exposure to ultraviolet radiation have been studied in the case of 30/4 mercerized bleached cotton and of 150-denier, 40-filament textile viscose rayon.

Experimental Procedure

The nitrating mixture used is prepared essentially according to the technique of Herrent and Govaerts [6]. It is composed of 47% nitric acid, 33% phosphoric acid, and 20% phosphoric anhydride by weight. The nitrating mixture is prepared by adding the required amount of phosphorous pentoxide to the phosphoric acid, meanwhile cooling the mixture to maintain it at 15°–20°C. The fuming nitric acid is then added slowly, with agitation. The nitrating solution is stored in an amber glass-stoppered bottle at 20°–22°C. It is stable under these storage conditions, and will keep for extended periods of time. All chemicals used are of reagent grade: 70% fuming nitric acid (specific gravity, 1.49–1.50), 85% orthophosphoric acid (specific gravity, 1.68–1.69), and powdered phosphorous pentoxide.

The selected sample is prepared in the form of a fine fluff by cutting. It is dispersed in distilled water, with vigorous agitation, collected in a loose pad on a fritted-glass filter disc, and dried at 105°C to constant weight. A 2-g. portion is then nitrated with a 100:1 weight ratio of the nitrating mixture at 20°C for a period of 1 hr.

Nitration is stopped by removal of the acid mixture by suction on a fritted-glass filter, followed by "drowning" on the filter with cold water. The sample is then stabilized by a 10-min. boil in distilled water, recovered by filtering, and dried at room temperature under vacuum.

For fractionation, 200 ml. of a 0.5% solution is prepared in 95% acetone. Precipitation is brought about initially by addition of distilled water to the solution at 20°C. The water is added dropwise with gentle agitation, until a marked turbidity develops in the system. The complete system is then warmed to approximately 30°C, at which condition the precipitate is redissolved completely. The fraction is reprecipitated by slowly cooling the solution back to 20°C. After 15 min. at this temperature, the precipitate is allowed to settle, and the supernatant liquid is decanted. The same sequence of diluent addition and warming, followed by cooling and reprecipitation, is followed for the separation of the subsequent fractions.

The precipitate is freed of excess liquid by suction-filtering, followed by a wash with 20% acetone and a wash with distilled water. Preliminary drying is on a steam bath, followed by final drying at room temperature under vacuum.

Ten fractions are usually taken from each sample —nine by precipitation, and the tenth by evaporation of the final supernatant solution. Experience has indicated that it is desirable to prepare fractions of a fairly even size, judged by the visual appearance of turbidity in the precipitation system. Recovery of 95% or better of the initial sample is normally obtained.

The nitration technique described here results in a nitrate of between 13.20% and 13.50% nitrogen content. No significant change in nitrogen content is noticeable within the various fractions drawn from one sample nitration.

Viscosity determinations are carried out on each fraction in order to determine the average degree of polymerization of each one. The usual viscometric solution is one containing 0.05 g. of cellulose nitrate per 100 ml. of solution in 95% acetone. Viscosities are measured at 20°C with a Cannon-Fenske viscometer.

Viscosities obtained are used to calculate intrinsic viscosities by the Schulz-Huggins equation [8, 18]:

$$[\eta] = \frac{\eta_{sp}}{c(1 + K\eta_{sp})},$$

where

$$\eta_{sp} = \frac{\eta_{soln} - \eta_o}{\eta_o},$$

c is concentration in g./100 ml., and K is a constant

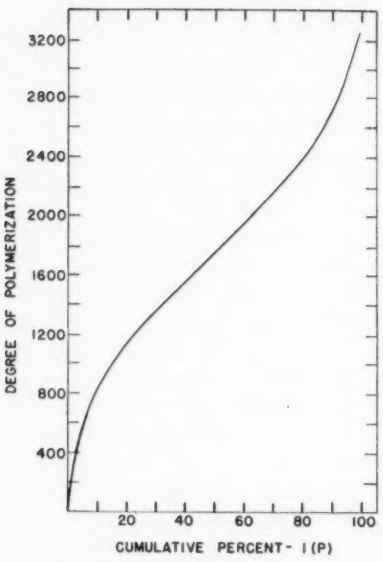

FIG. 1. *Integral distribution curve: pulped bleached cotton cellulose; 99% alpha-cellulose. Derivative—cellulose nitrate, 13.41% N; solvent—95% acetone; precipitant—distilled water.*

TABLE I. FRACTIONATION DATA: PULPED BLEACHED COTTON CELLULOSE*

Precipitated (%)	Summative (%)	$I(P)$	D.P.
8.7	8.7	4.3	550
11.4	20.1	14.4	990
12.1	32.2	26.2	1245
9.3	41.5	36.9	1510
10.4	51.9	46.7	1655
16.1	68.0	60.0	1970
11.4	79.4	73.7	2235
8.3	87.7	83.5	2470
6.1	93.8	90.8	2745
4.8	98.6	96.2	3030

* Alpha-cellulose content, 99%. Derivative—cellulose nitrate, 13.41% N; solvent—95% acetone; precipitant—distilled water.

equal to 0.315. The constant characterizes the polymer-solvent system in question, and is found to be moderately insensitive to minor changes in degree of nitration. Other well-known equations for this relationship could be utilized, such as Martin's [11], Philippoff's [16, 17], or Baker's [1].

The degree of polymerization is calculated from intrinsic viscosity by means of the revised Staudinger equation [9, 21]:

$$\text{D.P.} = [\eta] \times K,$$

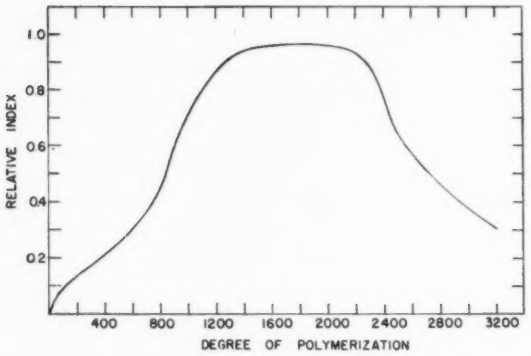

FIG. 2. *Differential distribution curve: pulped bleached cotton cellulose.*

TABLE II. DIFFERENTIAL PLOT DATA: PULPED BLEACHED COTTON CELLULOSE

D.P.	Slope (%/400 D.P.)	Relative index
200	2.5	0.13
400	4.0	0.20
600	6.5	0.33
800	8.5	0.43
1000	14.5	0.73
1200	17.0	0.85
1400	19.0	0.95
1600	19.0	0.95
1800	19.2	0.96
2000	19.0	0.95
2200	18.5	0.93
2400	14.0	0.70
2600	11.0	0.55
2800	8.5	0.43
3000	7.5	0.37
3200	6.0	0.30

where K is a constant equal to 94. The constant is characteristic for a given solvent-solute system and over an extended range of nitrogen contents.

Results

Distribution data may be presented in any of several forms. Most common are the integral distribution plot and the differential form derived from it. The integral plot has D.P. as ordinate and the integral distribution function $I(P)$ as abscissa. $I(P)$ is the sum of one-half of a given fraction plus the total of all fractions occurring before. This function assumes that chain lengths in any given fraction are symmetrically distributed about the mean value of chain length of the fraction. The $I(P)$ function is normally expressed in terms of percentage of the original sample recovered. Differential plot data is

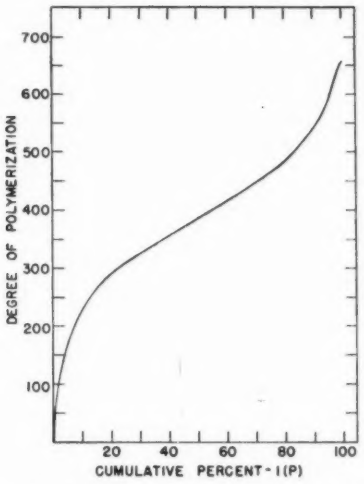

FIG. 3. *Integral distribution curve: tire cord viscose rayon from 100% wood pulp; 87% alpha-cellulose. Derivative—cellulose nitrate, 13.29% N; solvent—95% acetone; precipitant—distilled water.*

readily secured from this form by slope measurements on tangents to the curve taken at several points.

A useful variation of the integral distribution curve is a plot on probability paper, with $I(P)$ along the nonlinear abscissa. On such a plot, deviation from Gaussian distribution manifests itself as deviation from a straight line. It is useful because of the expansion of scales at extremes, thus bringing into greater prominence the important distribution of high and low D.P. fractions.

Table I gives fractionation data for a pulped bleached cotton cellulose of 99% alpha-cellulose content; the nitrated sample contained 13.41% nitrogen. Data are presented in Figure 1.

Differential plot data for the same material are given in Table II, with the data presented in Figure 2.

By comparison, Figure 3 presents integral distribution data for a tire cord viscose rayon from 100% wood pulp of 87% alpha-cellulose content; the nitrate sample contained 13.29% nitrogen. The differential plot of this same data is given in Figure 4. The distribution peak is seen to be narrower and sharper than that for the cotton cellulose.

Figure 5 presents the probability type of integral distribution plot for these two celluloses. From this type of plot it is easy to determine median D.P.—the intersection point of the 50% line. Likewise,

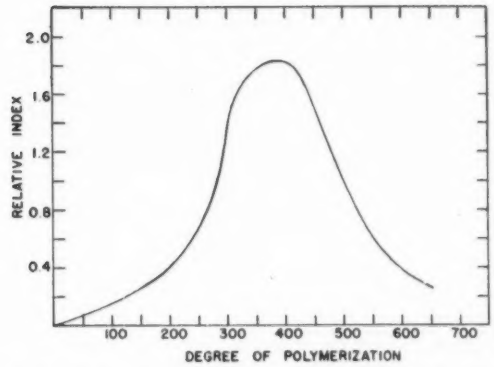

FIG. 4. *Differential distribution curve: tire cord viscose rayon from 100% wood pulp.*

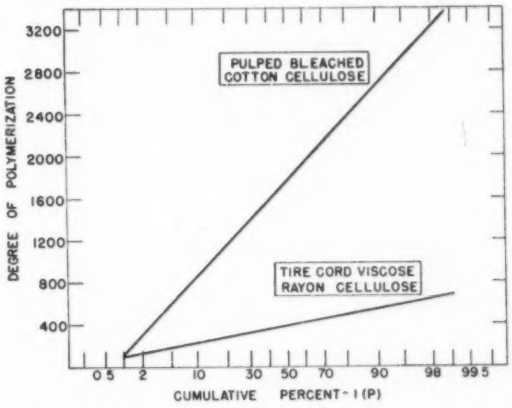

FIG. 5. *Probability form integral distribution curve: pulped bleached cotton cellulose and tire cord viscose rayon from 100% wood pulp.*

10% and 90% indices may be derived in the same manner from the intersection points for these values. These indices are convenient as an indication of the heterogeneity of the sample in question.

Samples of a normal cotton cellulose which have been exposed to degradative action show marked differences in distribution of D.P. as well as in average D.P. value. For example, let us look at data on normal mercerized bleached 30/4 cotton, before and after exposure to weathering, as given in Figure 6. This material has an average D.P. of 1430, which is normal for commercial Egyptian cotton, after mercerization and bleaching.

The original material shows a very nearly Gaussian distribution of degree of polymerization. After 500 hrs. of exposure in a Single Arc Weatherometer,

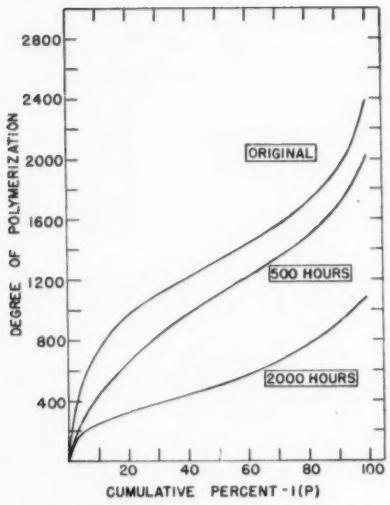

FIG. 6. *Integral distribution curves: 30/4 mercerized bleached cotton, before and after Weatherometer exposure. Derivatives—cellulose nitrates, 13.27%–13.33% N; solvent—95% acetone; precipitant—distilled water. Periods of exposure in Atlas Single Arc Weatherometer are given.*

this material has lost approximately 11% of its strength, and shows a marked drop in average D.P. The entire curve of D.P. distribution shows a lowering, with an average D.P. of 1180, but with little change of distribution form. Exposure for 2,000 hrs. results in a strength loss of 34%, and an average D.P. of 570. The integral distribution curve now shows marked alteration in shape, with a much higher percentage of low D.P. material.

The same facts are borne out by the integral distribution curves on probability paper, as seen in Figure 7.

It is evident that the distribution changes here manifest themselves as changes in slope and in deviation from linearity. The relation of 10% and 90% indices to the median value of D.P. also shows marked change.

In the original material, the 10%–90% range was 0.887 of the median value. After 500 hrs. of exposure, the 10%–90% range has increased to 1.093 of the median; and after 2,000 hrs. of exposure, the range has risen to 1.232 of the median value.

The same type of differences are noticeable in studies of a textile rayon exposed to ultraviolet irradiation. A 150-denier, 40-filament viscose rayon was also exposed in a Single Arc Weatherometer;

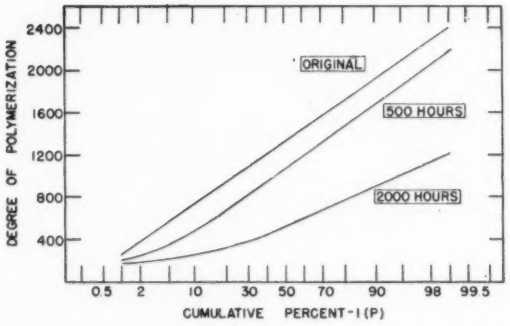

FIG. 7. *Probability form integral distribution curves: 30/4 mercerized bleached cotton, before and after Weatherometer exposure.*

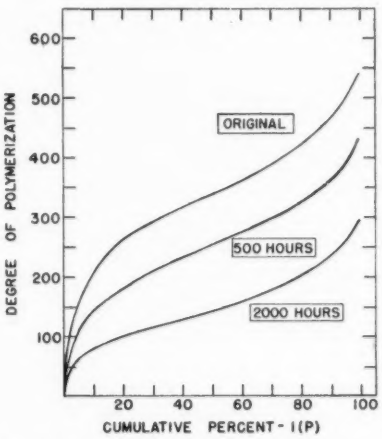

FIG. 8. *Integral distribution curves: 150-denier, 40-filament textile viscose rayon, before and after Weatherometer exposure. Derivatives—cellulose nitrates, 13.34%–13.44% N; solvent—95% acetone; precipitant—distilled water. Periods of exposure in Atlas Single Arc Weatherometer are given.*

data obtained in this experimental run followed a similar pattern, as illustrated in Figure 8.

Again, an essentially Gaussian distribution is found in the original material, with a mean degree of polymerization of 376. Exposure for 500 hrs. causes a drop of 17% in strength, and a resulting average D.P. of 289. Exposure of a sample for a total of 2,000 hrs. results in a strength loss of 41% and a drop in average degree of polymerization to 173. Barely perceptible alteration of the integral distribution pattern is present after 500 hrs. of exposure, but this change becomes quite marked after the 2,000-hr. period.

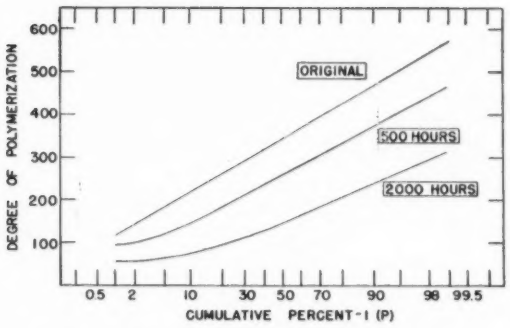

FIG. 9. *Probability form integral distribution curves: 150-denier, 40-filament textile viscose rayon, before and after Weatherometer exposure.*

The probability type of integral plot, given in Figure 9, again emphasizes these facts quite clearly.

Discussion and Conclusions

A most interesting fact is brought forth in these sets of data. The degraded celluloses both exhibit minor distribution peaks at the lower D.P. end of the scale. This low D.P. concentration occurs in the neighborhood of 235 D.P. for cotton cellulose and at approximately 76 D.P. for degraded cellulose from viscose rayon. These values are in substantial agreement with the values for "limit cellulose" as presented by Mehta and Pacsu [12]. Their values were D.P. 256 for cotton cellulose and D.P. 64 for regenerated celluloses. These are the limiting values derived by mild acidic hydrolysis of cotton cellulose and regenerated cellulose.

Whether or not the occurrence of these minor distribution peaks in the ultraviolet-degraded cellulose is open to the same or to an analogous interpretation as Mehta and Pacsu's [12] data is problematical. Nevertheless, the occurrence of similar peaks at approximately the same points in the D.P. range does present a striking analogy still to be investigated.

Acknowledgment

The author wishes to express his gratitude to all members of the Research Division staff of the Belding Heminway Company who have contributed to this study.

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(*Manuscript received April 16, 1952.*)

The Effect of the Degree of Polymerization on the Serimetric Properties of Regenerated Cellulose Fibers*

J. R. Coley†

IN the manufacture of rayon by the viscose process the average degree of polymerization (D.P.) of the native cellulose for typical operation is reduced from approximately 1000 to 350. This extensive degradation is not inherent in viscose processing, but is a carefully controlled step to give a spinning solution that will present the minimum in mechanical difficulties. The extent of degradation can be reduced a substantial amount before mechanical difficulties, due largely to greatly increased viscosity of the spinning solution, become excessive. Production of rayon with an average D.P. of 500–600 is possible by reduction of the degradation; however, there is a diversity of opinion as to whether this increase in D.P. is accompanied by a sufficient increase in tensile strength to warrant the added technical difficulties encountered. Lauer and Doderlein [2] reported that above 220 the degree of polymerization has no effect on tensile strength and stretch. However, Schwarz and Wannow [3] concluded from comparison of the tensile strength of fibers varying in average D.P. from 290 to 480 that a D.P. of approximately 430 gives the optimum tensile properties. The experimental data reported herein on the variation of tensile strength with D.P. were obtained in an effort to clarify this problem.

Experimental

The D.P. of the regenerated cellulose was varied by changing the aging time of the alkali cellulose from 19 to 163 hrs. Thirteen batches of different aging times were converted into rayon by a procedure closely paralleling commercial practice; the various operations were carried out in pilot-scale equipment under essentially constant conditions.

Batches of 780 g. of spruce sulfite sheets were steeped in 18.0% sodium hydroxide for 60 min. at 20°C, pressed to 3.0 press ratio, and shredded for 135 min. at 20°C. The resulting alkali cellulose crumbs were aged at 18°C, xanthated for 180 min. at 25°C, with an amount of 31% CS_2 based on the cellulose in the alkali cellulose, mixed to give a viscose containing 7% cellulose and 6.5% NaOH, ripened at 18°C to an 8.0 NH_4Cl ripeness number, and spun into a bath maintained at 45°C and composed of 9.8% H_2SO_4, 18.1% Na_2SO_4, 3.8% $MgSO_4$, and 1.0% $ZnSO_4$.

Each batch consisted of six bobbins, each spun at a different draft. The draft, which is defined as the ratio of rate of viscose withdrawal to rate of expulsion, ranged from 1.1 to 4. The variations in draft, or stretch, were produced by decreasing the rate of expulsion of the viscose while maintaining a constant rate of withdrawal. In this way it was possible to keep the immersion time constant. The rayon was spun under 30 g. tension applied by means of an adjustable thread guide. The rayon was water-

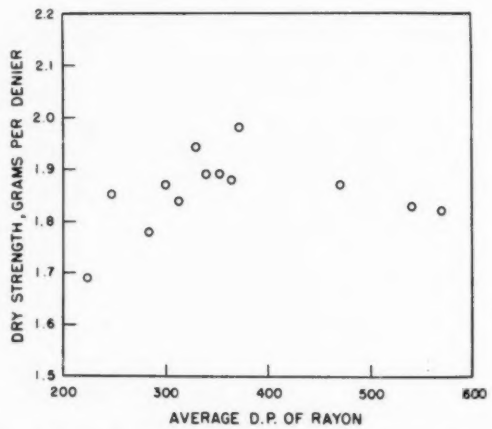

FIG. 1. *Dry strength of rayon spun at draft of 2.0 versus average D.P. of rayon.*

* From a portion of the dissertation submitted by J. R. Coley to Georgia Institute of Technology, Atlanta, Ga., in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering, June 1939.

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TABLE I. THE EFFECT OF THE DEGREE OF POLYMERIZATION ON THE SERIMETRIC PROPERTIES OF REGENERATED CELLULOSE FIBERS

Aging time (hrs.)	19	36	43	61	67	84	92	108	115	132	139	156	163
Average D.P.													
Crumbs	605	584	498	457	440	408	358	387	334	390	313	330	280
Rayon	540	570	470	372	365	340	351	330	312	300	248	283	222
Dry strength (g./den.)													
Spun at 2.0 draft	1.83	1.83	1.87	1.98	1.88	1.89	1.89	1.94	1.84	1.87	1.85	1.78	1.69
Spun at 3.0 draft	2.02	1.94	2.12	2.05	2.08	1.87	2.06	2.02	1.84	1.94	1.98	1.87	1.73
For a 10.0% dry elongation	1.82	1.82	1.80	1.92	1.77	1.89	1.70	1.87	1.67	1.80	1.59	1.65	1.50
Wet strength (g./den.)													
Spun at 2.0 draft	0.75	0.77	0.78	0.87	0.78	0.80	0.75	0.84	0.73	0.81	0.72	0.72	0.64
Strength loss when wetted (%)													
Spun at 2.0 draft	59.0	58.0	58.3	56.6	59.1	57.7	60.3	58.8	60.3	56.7	61.1	59.5	62.2

washed, air-dried, and tested without desulfurization. The desulfurization step was omitted because slight variation in the concentration of the desulfurization solution would produce changes in the properties of the yarn and introduce an undesirable variable.

The rayon was twisted to 2.5–3.0 turns per inch. The twisted rayon was then reeled into four skeins 225 m. long, conditioned at 65% relative humidity, and weighed for denier determination; the third skein was used for breaking strength determinations. The number of breaks made on each skein varied with the uniformity of the yarn. The average deviation from the mean breaking strength allowed was 1.5 g.

The average D.P. values of the alkali cellulose crumbs and of the rayon were determined from measurements of the viscosity of dilute solutions in cuprammonium hydrate. The Clibbens and Geake method [1], modified to insure the absence of any contact between air and the cuprammonium solution, was employed. The value of K_m in the equation $\eta_{sp}/c = K_m M$ used for converting fluidities to D.P was 5×10^{-4}.

Results and Discussion

Variation of the alkali cellulose aging time from 19 to 163 hrs. produced a variation in the average D.P. of the rayon from 570 to 222. The experimental data are summarized in Table I. Graphical representation of the variation of dry strength obtained at spinning drafts of 2 and 3 with average D.P. (Figures 1 and 2) indicates an optimum D.P. in the range of 375–450. The tensile strength in-

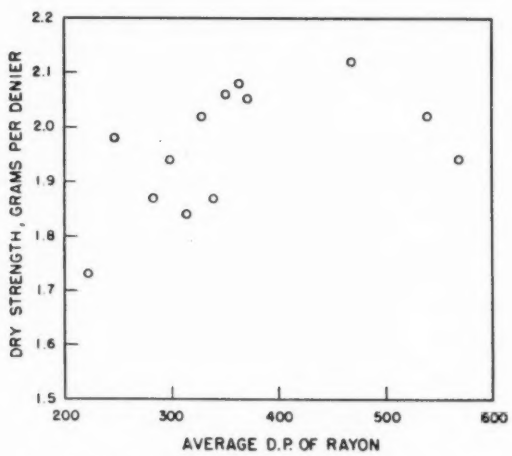

FIG. 2. *Dry strength of rayon spun at draft of 3.0 versus average D.P. of rayon.*

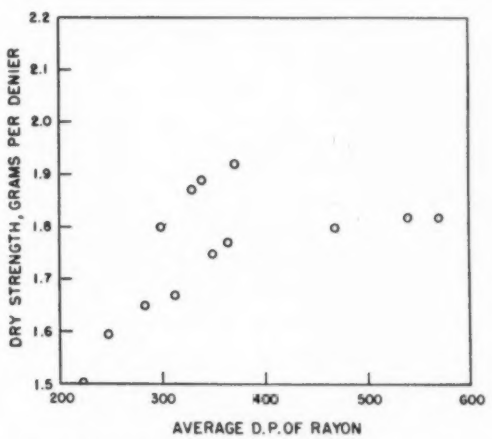

FIG. 3. *Dry strength at dry elongation of 10% versus average D.P. of rayon.*

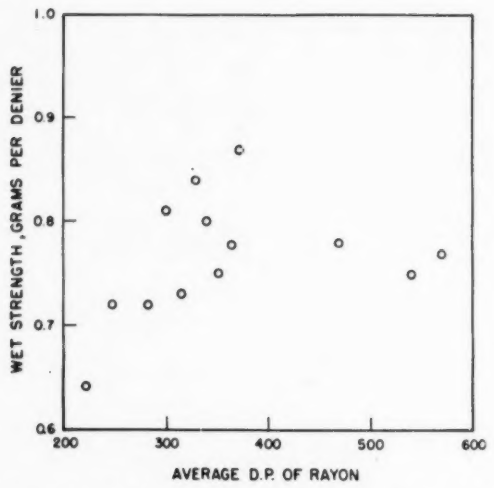

FIG. 4. *Wet strength of rayon spun at draft of 2.0 versus average D.P. of rayon.*

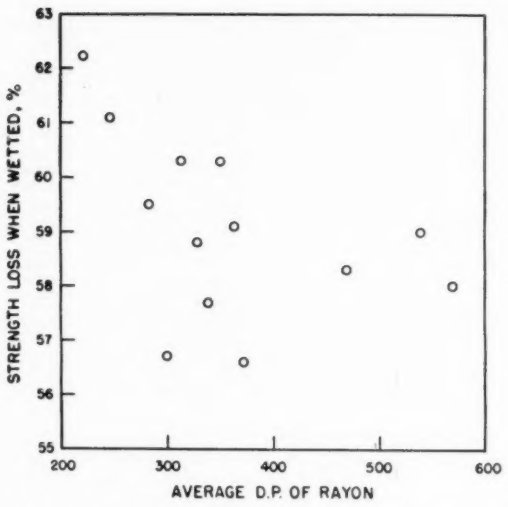

FIG. 5. *Strength loss when wetted of rayon spun at draft of 2.0 versus average D.P. of rayon.*

creases linearly with the draft. However, the amount of draft that can be applied practically is limited because dry elongation decreases linearly with increased draft, and rayon with less than 10% dry elongation causes difficulties during processing on textile machinery. The draft necessary to give a 10% dry elongation was in the range of 2–3. The dry strength obtained at 10% dry elongation was found by plotting dry strength *versus* dry elongation. The variation of dry strength at 10% elongation *versus* D.P. is shown in Figure 3. The optimum D.P. (375–425), as determined from Figure 3, differs only slightly from that indicated in Figures 1 and 2. A plot of wet strength *versus* D.P. (Figure 4) also gives the same D.P. optimum (375–425). The variation of strength loss when the rayon is wetted *versus* D.P. (Figure 5) indicates that the loss drops steadily with increased D.P. until the range 375–400 is reached, after which the strength loss is independent of D.P. variation.

Thus, it appears that an increase in the D.P. above the range of 375–425 produces no beneficial changes in the tensile properties of the rayon fibers. Although the tensile properties of the fibers reported are below those of an acceptable commercial product, as might be expected in comparison of a pilot-scale product with a commercial product, it is felt that the differences in tensile properties reported are real and that the conclusions drawn on tensile strength variation with D.P. are justified.

Acknowledgments

The author wishes to thank Nathan Sugarman of the Georgia State Engineering Experiment Station for his helpful suggestions, and the Experiment Station for the use of pilot-scale viscose processing equipment.

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(Manuscript received October 6, 1952.)

Distortion in Knit Fabrics and Its Relation to Shrinkage in Laundering

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Abstract

The dimensional changes in laundering of 15 fabrics knit from cotton, viscose, acetate-viscose, and nylon yarns were investigated in relation to changes in fabric structure. The fabrics included plain and rib knit of 24, 28, 32, 36, 40, and 44 courses per inch, and interlock knit of 24, 28, and 32 courses per inch. The geometry of both finished and gray fabrics before and after laundering was compared to the geometry of the same fabrics which had received a manual relaxation treatment. Measurements of wale and course spacings showed that laundering brought about considerable rearrangement in the structure of the fabrics which had not been relaxed. The data for wale *versus* course spacings followed parabolic curves for the laundered fabrics and for all relaxed fabrics. The relation of the course spacings before and after laundering and of the wale spacings before and after laundering was linear for the fabrics given the relaxation treatment. Dimensional change in length, width, and area of the relaxed fabrics was usually not greater than 10%, and often less than 5%. Changes in area varied markedly with the knitting stiffness of the finished fabrics, but after relaxation treatment, the changes were small and were not influenced by the knitting stiffness.

DISTORTION of knit goods is inherent in their manufacture. Spiraling effects are common since there can be no widthwise alignment of circular knit goods, and since tension is automatically controlled only in the lengthwise direction as new loops are added. Because the knit cloth is a series of loops, a complete change may occur in the shape of the unit cell when the fabric is released from the tension of the machine. However, other stresses and strains have been set up which can be released only by wetting out and agitation of the free fabric.

When gray fabrics are finished, they frequently are not stretched widthwise sufficiently to bring them to a stable arrangement. The relationship of wale and course spacings is disregarded, and all fabrics knit on the same machine are often finished to approximately the same width. In many fabrics, therefore, the dimensions may change excessively when they are laundered.

The study reported here was undertaken to investigate rearrangements in structure during the laundering of plain, rib, and interlock knit fabrics made from cotton, acetate, viscose, and nylon. Comparisons of structure were also made of the fabrics with and without a prior manual relaxation treatment.

Materials

The fabrics studied were the same as those used in a previous study of geometry in relation to shrinkage [2, 3]. They were knit under controlled conditions in the Textile Research Department of the American Viscose Corporation. The cotton fabrics were knit of medium staple 30/1 combed Peeler; the rayon and nylon fabrics, of 30/1 yarn spun from 1.5-in. staple fibers. The yarns included (*1*) bright viscose rayon, 1.5 denier; (*2*) a blend of 50% dull acetate and 50% bright viscose, 2.0 denier; and (*3*) bright nylon, 1.5 denier. All the yarns had a Z twist of approximately 18 turns per inch.

Six plain and six 1 × 1 rib fabrics were knit from each yarn in 24, 28, 32, 36, 40, and 44 courses per inch. Only three interlock materials of each yarn—24, 28, and 32 courses per inch—were knit because it was impossible to make fabrics of a higher number of courses with these yarns on the knitting machine used.

Method

Since there is no standard test method for the shrinkage in laundering of knit goods, the proce-

dures for A.A.T.C.C. standard methods for woven cloth were used [1]. Temperatures of 212°–140°F were maintained for cotton, and 100°F for the rayons and nylon. After the last rinse, each specimen, without tension, was floated in water over a wire screen placed on the bottom of a tray. Both the fabric and the screen were lifted from the tray. The material was not removed from the screen until it was dry.

One set of three specimens, 15 inches square, was used to obtain data on dimensional change in five launderings for each gray and each finished fabric. Another set of specimens was subjected to manual manipulation, which was intended to reduce spiral effects and to bring wale and course spacings into relationships approximating those of the laundered fabric.

The manual manipulation, or relaxation treatment, consisted of stretching or shrinking the cloth, which had been soaked in warm water for 2 hrs., to approximately the dimensions assumed by a similar area of the laundered fabric. The material was then floated over a screen and allowed to dry without tension. Care was necessary to prevent the material from hanging over the edge of the screen or lying in folds heavy enough to prevent shrinkage during drying. Gray fabrics were laundered once to remove oil and other dressing and then dried before they were soaked and relaxed. The treated specimens were then marked and laundered five times.

Wales and courses of each fabric were counted before and after laundering. Stitch length and diameter of the yarns were measured as described in a former study [2]. All counting and measuring was done on the conditioned specimens at 65% relative humidity and 70°F.

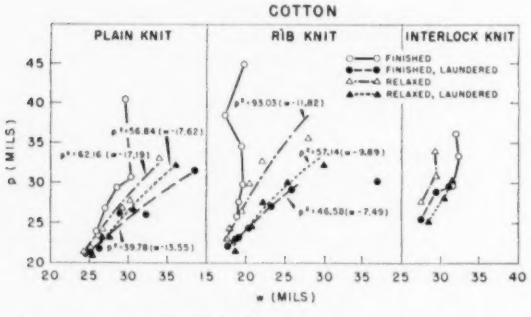

FIG. 1. *Relationship of wale* (w) *and course* (p) *spacings of laundered (five times) and unlaundered knit cotton fabrics before and after relaxation treatment.*

Results and Discussion

Cotton Fabrics

Before the finished cotton fabrics were laundered, the relation of course spacings to wale spacings followed no regular pattern, but after laundering, the data approximated parabolic curves (Figure 1). These differences indicate distortion in the structure of the unlaundered fabric.

Figure 1 also shows the relationship of wale and course spacings of the relaxed fabrics before and after laundering. The data for the plain and rib knit materials follow parabolic curves similar to those of the laundered untreated fabrics. The quadratic equations of these parabolic curves show that the intercepts of the w-axis range from one to two yarn diameters (diameter = 8.725 mils).

The data of the wale and course spacings of the interlock fabrics are similar to those of the plain and rib knit. However, since only three of these materials were available, no attempt was made to fit the data to curves.

Further evidence of distortion in the finished unlaundered fabrics is found in the relationship of the course spacing before laundering, p_o, to course spacing after laundering, p_1, and of wale spacing before laundering, w_o, to wale spacing after laundering, w_1 (Figure 2). In the case of the relaxed fabrics, however, both these relationships are found to be linear,

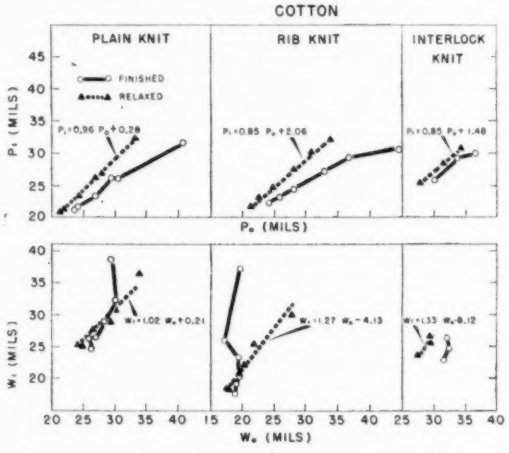

FIG. 2. *Relationship of wale spacings* (w) *before and after laundering and course spacings* (p) *before and after laundering of finished and relaxed cotton fabrics.* w_o *and* p_o *indicate spacings before laundering;* w_1 *and* p_1 *indicate spacings after laundering.*

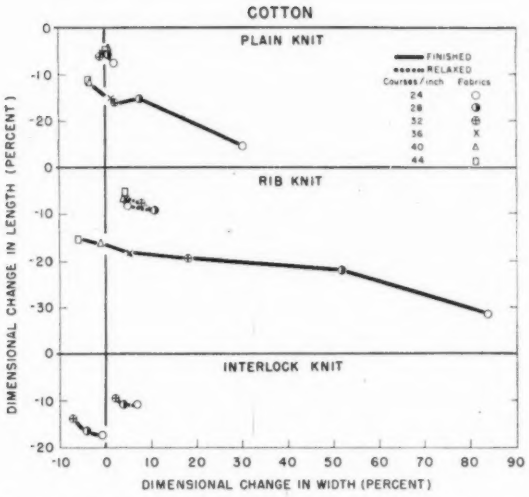

FIG. 3. *Dimensional change in five launderings of knit cotton fabrics before and after relaxation treatment.*

indicating that the changes in the shape of the unit cell were similar in both the tightly knit and the loosely knit materials (Figure 2). The measured changes in length and width of the fabric after five launderings confirm this point.

Changes in dimensions in laundering of all of the cotton goods were smaller for the relaxed fabrics than for the cloth not given a relaxation treatment (Figure 3). For example, the untreated plain knit fabric with 24 courses per inch stretched 30% in width and shrank 25% in length. Similarly, the untreated rib knit fabric with 24 courses stretched 83% in width and shrank 32% in length. On the other hand, the shrinking and stretching of the relaxed fabrics never exceeded 11%, and for several materials was not more than 5%. Comparison of these results with similar data reported earlier for fabrics treated by three different mechanical processes shows that the laboratory relaxation treatment gave more satisfactory performance for the loosely knit goods [2]. The plain fabric of 24 courses per inch treated by the best of the mechanical finishes shrank 13% in length and stretched 17% in width; the rib fabric shrank 14% in length and stretched 45% in width.

The change in area of the laundered relaxed fabrics was small, ranging from 0% to 8% (Figure 4). This is a considerable improvement over the unrelaxed materials. The tightly knit fabrics of the latter group shrank 15% to 20% in area. Shrinkage for the tightly knit cloth was significantly more than that for the loosely knit materials. In the case of the rib knit, the excessive widthwise stretching resulted in an increase in area of as much as 25% in loosely knit materials.

Experimentation with the gray fabric shows that curves plotting wale spacings against course spacings of the relaxed gray materials are also parabolic. Figure 5 shows that the relationship for the wale and course spacings of the relaxed plain knit gray goods is nearly identical with that of the relaxed finished fabrics.

Loosely knit gray and finished fabrics often exhibit considerable progressive change in dimensions during laundering. The graphs in Figure 6 show how the shrinkage in length and the stretching in width increased with each successive laundering. On the other hand, the relaxed materials did not shrink progressively in laundering. The relaxed gray fabric

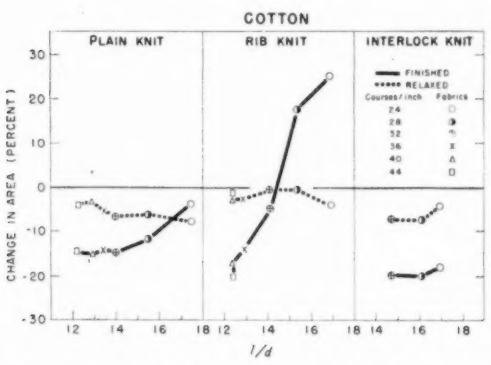

FIG. 4. *Relationship of change in area in five launderings to cover factor, stitch length/yarn diameter (l/d), of cotton fabrics before and after relaxation treatment. Diameter of yarn = 8.725 mils.*

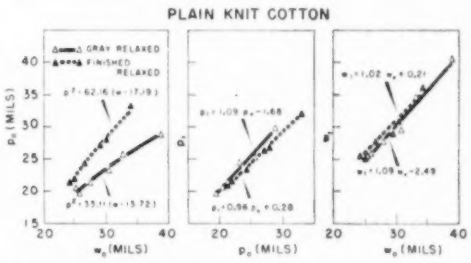

FIG. 5. *Relationship of wale (w) and course (p) spacings of relaxed gray and finished plain knit cotton fabrics.* p_o *and* w_o *indicate spacings before laundering;* p_l *and* w_l *indicate spacings after laundering.*

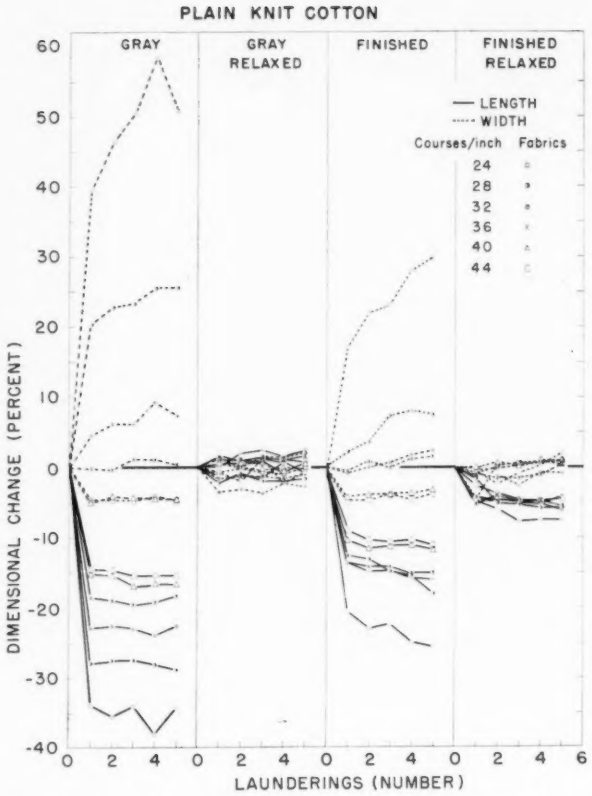

FIG. 6. *Dimensional change in successive launderings of gray and finished plain knit cotton fabrics.*

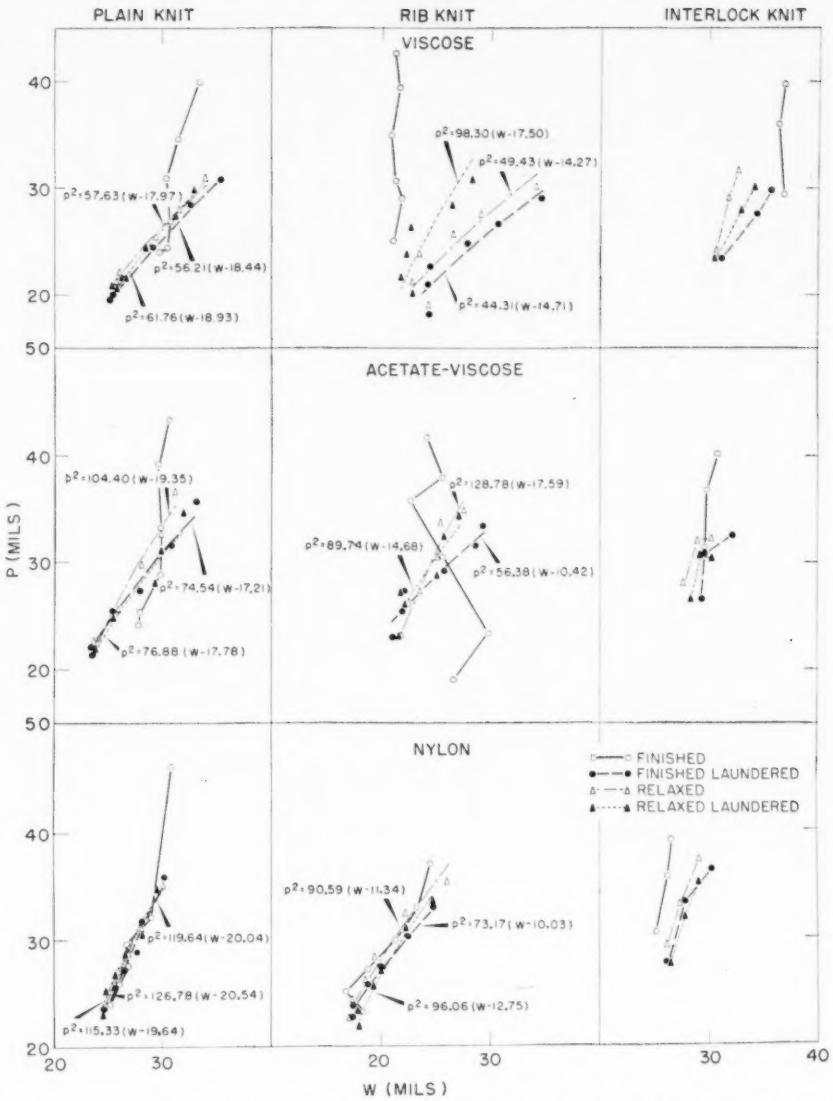

FIG. 7. *Relationship of wale (w) and course (p) spacings of finished and relaxed rayon and nylon fabrics before and after five launderings.*

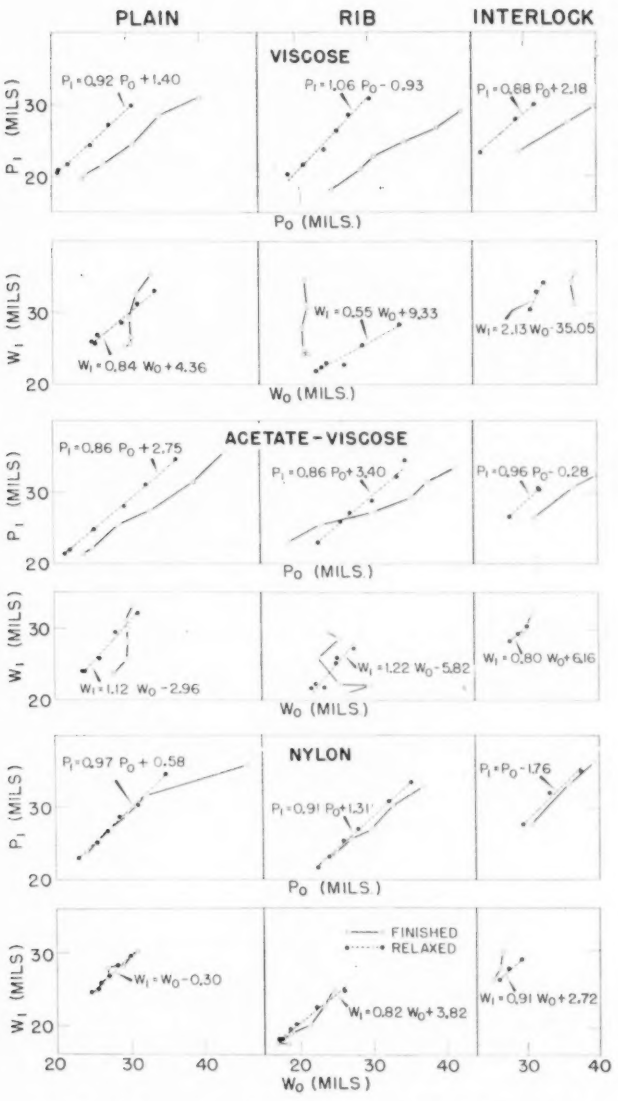

FIG. 8. *Relationship of wale spacings (w) before and after laundering and of course spacings (p) before and after laundering of finished and relaxed fabrics of rayon and nylon.* w_o *and* p_o *indicate spacings before laundering;* w_1 *and* p_1 *indicate spacings after laundering.*

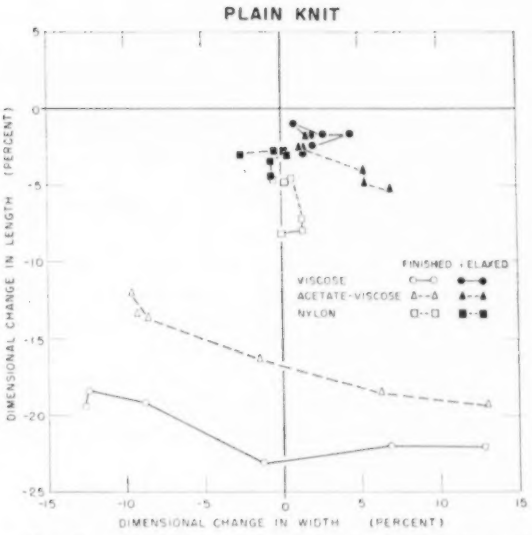

FIG. 9. *Dimensional change in five launderings of plain knit rayon and nylon fabrics before and after relaxation treatment.*

FIG. 10. *Relationship of change in area in five launderings to cover factor, stitch length/yarn diameter (l/d), of plain knit rayon and nylon fabrics before and after relaxation treatment. Diameter of yarn equals experimental values [3].*

stretched and shrank less than the same material which had been finished and then relaxed.

Rayon and Nylon

The rearrangement of the fabric structure during laundering of the rayons and nylon was similar to that of the cotton fabrics (Figures 1, 2, 7, and 8). Likewise, the relaxed fabrics showed little structural rearrangement in laundering.

The dimensional changes in the length and width of the relaxed rayons and nylon knit goods were considerably less than for the unrelaxed materials. For example, as shown in Figure 9, the plain knit viscose rayon shrank in length from 18% to 23% and in width the change varied from 13% shrinkage to 13% stretch. The relaxed viscose fabric shrank or stretched less than 5%.

For the viscose fabrics, as for the cotton, the dimensional change in area during laundering increased as the knitting stiffness increased (Figure 10). On the other hand, for the acetate-viscose and for the nylon, the dimensional change in area decreased as the knitting stiffness increased. After relaxation, however, the change in area was small and was not influenced by knitting stiffness.

Summary

In brief, the results of this investigation show that changes in dimensions of knit goods in laundering are due largely to a rearrangement of the fabric structure. It was demonstrated that the fabrics could be given a relaxation treatment to remove distortion so that the structure would exhibit little rearrangement after laundering and the area would remain nearly constant.

When the materials were given this treatment, the wale spacings *versus* the course spacings followed a parabolic curve, and little dimensional change occurred in the laundered fabric. For the relaxed fabrics, dimensional changes usually were not greater than 10%, and often were less than 5%. The relation of area change to variations in knitting stiffness was marked in the finished fabrics, but after relaxation, changes in area were small and were not influenced by knitting stiffness.

Acknowledgment

Grateful acknowledgment is made to Elinora Dent for laboratory assistance, and to Mary A. Fajen for laboratory assistance and for aid in preparation of the data reported in this paper.

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(*Manuscript received October 27, 1952.*)

A New Method of Producing the Allwörden Reaction

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THE FORMATION of bubbles or blisters on the surface of wool fibers and other animal hairs following their immersion in chlorine water was discovered by K. von Allwörden in 1913 and since that time has aroused continued interest. Various authors advanced the view that the bubbles are bounded by a thin skin and that the inflation is an osmotic phenomenon [2]. Müller's experiments [5] did much to establish this view, and the isolation of a thin membrane from the "Allwörden sacs" by Lindberg [3] provided convincing evidence. From its position external to the cuticle of the fiber this thin membrane is now known as the "epicuticle."

The Allwörden reaction also takes place in solutions of bromine but not in those of iodine. If the current explanation is correct, the reaction might be expected to occur in other instances where an osmotically active decomposition product has been produced from the scaly layer without perforation of the membrane itself. Peracetic acid is known to destroy the disulfide cross-linkages of keratin and to render the altered keratin soluble in alkaline media. Alexander has shown that such oxidized fibers quickly dissolve in ammonia leaving a peripheral resistant remnant [1]. In a study of this reaction at lower pH values, it was found that the Allwörden blisters appear when the oxidized fibers are treated in aqueous solutions of pH about 8.

Wool was carefully cleaned with solvents and treated for 24 hrs. in a 1% peracetic acid solution. The oxidized fibers were then washed in water and finally treated with 1% sodium bicarbonate solution (pH 8–8.3). Bubbles began to form at once, appearing first on each single scale face and then running together to form larger bubbles which extended over the area of several scales, as is also the case with the chlorine-induced bubbles. In the microphotographs (Figure 1) many aspects of the phenomenon may be seen.

The fibers swell in the mildly alkaline medium and a certain amount of protein enters solution. This matter will be discussed elsewhere. On standing for some minutes, a more or less complete fusion of the individual bubbles occurs and the swollen fiber appears to be enclosed in a continuous tube. This development is hastened when the pH is raised. When the oxidized fibers are treated in the first place with

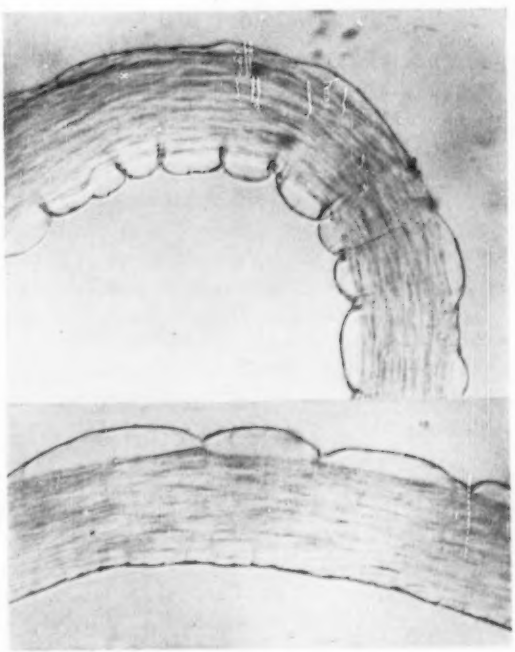

FIG. 1. *Bubble formation produced by treating oxidized wool fibers with 1% sodium bicarbonate. The primary single bubbles and their coalescence to form a continuous sheath may be seen.*

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solutions of high pH, the same sequence of events takes place with greater rapidity, and there remain only the external sheath, derived from the epicuticle, and some resistant remnants of cortical cells.

The bubbles produced on untreated wool in acid solutions of chlorine or bromine also tend to run together, but the fiber as a whole is not dissolved. However, when such a fiber exhibiting a "normal" reaction is transferred into media of increasing alkalinity, swelling is more marked, the bubbles run together, and a continuous tube is formed as before. This observation was also made by Müller.

The study of bubble formation by this new method has cast light on two questions concerning the peripheral structures of animal hairs. The first concerns the origin of the resistant tubules which remain when hairs are partly dissolved. Alexander [1] has asserted that in the case of fibers oxidized with peracetic acid the resistant tubule is actually a subcuticular structure; one of the present authors has maintained that the most obvious tubular component originates from the external layers of the cuticle. The slow development of bubbles and their conversion into a continuous tube, as can be seen in Figure 1, is evidence for the correctness of the latter view. There always remains within the tubes, however, a resistant remnant derived from the cortex, and this may represent Alexander's membrane, although its cortical origin and histology are very clear.

A second question has been: Is the epicuticle a continuous membrane entirely external to the cuticle, as asserted by Mercer, Lindberg, and Philip [4] (Figure 2*c*), or a cell membrane enveloping each flattened scale cell individually, as proposed by Zahn [6] following Müller [5] (Figure 2*a*)? The slow coalescence of the primary bubbles to form larger bubbles suggests very clearly the lifting off of a continuous external skin and is not easily reconciled with Zahn's view unless it is assumed that the membrane beneath the scales dissolves and the remnants on the external surface are fused into a continuous layer. Müller's experiments [5], which were cited by Zahn, led him to the view that the membrane is a genuine cell membrane. In the opinion of the present authors, his observations on the action of alkali on the Allwörden bubbles ([5], p. 28) and the action of chlorine on hairs previously digested by trypsin ([5], p. 38) and on plucked root ends ([5], p. 18) are better explained in terms of an entirely external epicuticle.

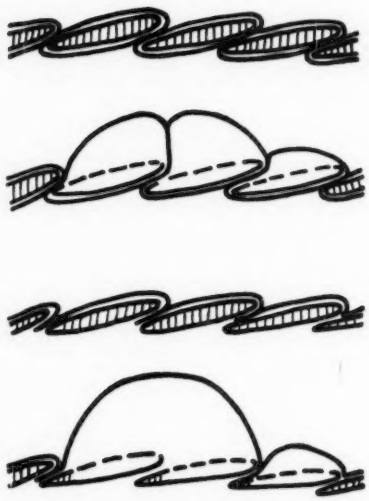

FIG. 2. *Two views of the course of the Allwörden reaction and the formation of compound bubbles. In* (a) *and* (b) *the epicuticle is supposed to envelop each scale cell individually. In* (c) *and* (d) *the epicuticle is a continuous external sheath. This latter view explains better the compound bubbles seen in Figure 1.*

The authors wish to express their gratitude to Dorothy O'Reilly for her help with the photography.

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(*Manuscript received October 28, 1952.*)

Corrugated Fibrous Webs as Insulation Fillers*

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Introduction

The Mellon Institute project on garment filling materials was initiated by the Office of The Quartermaster General in order to develop an improved batting type of insulation interliner for use in cold-climate clothing and possibly for sleeping bags. The best available low-density material at the time of the project's inception was characterized by good insulating properties but poor wear-resistance. Laboratory evaluation for simulated wear properties of insulation fillers, although not correlated thoroughly with field service data, soon demonstrated that practically all experimental materials were superior to this material.

In the same studies, modifications in fiber and batt form were found to yield fillers of increased compression-resistance as well as improvements in other features, giving superior insulation properties. Confirmation of these findings prompted a concentrated study of the experimental fibrous materials and of methods to improve the batt structures. Thus, while the initial concern was for durability of interliner materials, the program came to be broadened to include an investigation of the configuration of fibers, their compression-resistance, and their over-all insulation efficiency. One development stemming from these studies is the corrugation process—a fiber web-forming technique by which any fiber mass may be converted into a geometric form which provides high compressional resistance and good over-all insulation properties.

Garment Insulation Fillers

Clothing provides insulation primarily because it traps air. For conventional fibrous types of insulation, particularly for those of the same fiber size and type, the insulation efficiency may usually be considered to be approximately proportional to the thickness. This interdependence of thickness and insulation values is especially significant in military cold-climate clothing. The severe wear and/or excessive constant compressive loads applied to a Service garment frequently lead to appreciable temporary or permanent reduction in thickness and, consequently, in insulation value. Resistance to compression, therefore, is one of the important requirements of an efficient, cold-climate garment interliner.

Fiber and Fiber Forms

The stress-strain properties of fibers are important in estimating fiber resiliency. The latter property is a measure of the fiber's effectiveness in an interliner, particularly when prepared by the conventional laminated web process. But the influence of fiber and batt form is so important that a less resilient fiber in an improved form may actually surpass in insulation effectiveness an extremely resilient fiber formed in a less effective manner.

The influence of the properties of a particular fiber on insulation efficiency, furthermore, is more significant than can be explained on a basis of resiliency alone. Fiber diameter and fiber shape affect thermal conductivity and compression-resistance. For optimum insulation properties, it is ordinarily advantageous to select fibers possessing the most resilient properties and to blend mixtures of highly crimped fibers to achieve a structure wherein the interstices are such that a very low coefficient of thermal conductivity is afforded.

The value of crimped over straight filaments in improving loftiness of fibrous battings has been demonstrated, and further improvement in compressional resiliency has been attained through the use of "helix-shaped" fibers.

Conventional Batt Structure

The most common fibrous insulation structure consists of superimposed carded or garnetted fibrous webs. Even though more uniform properties are

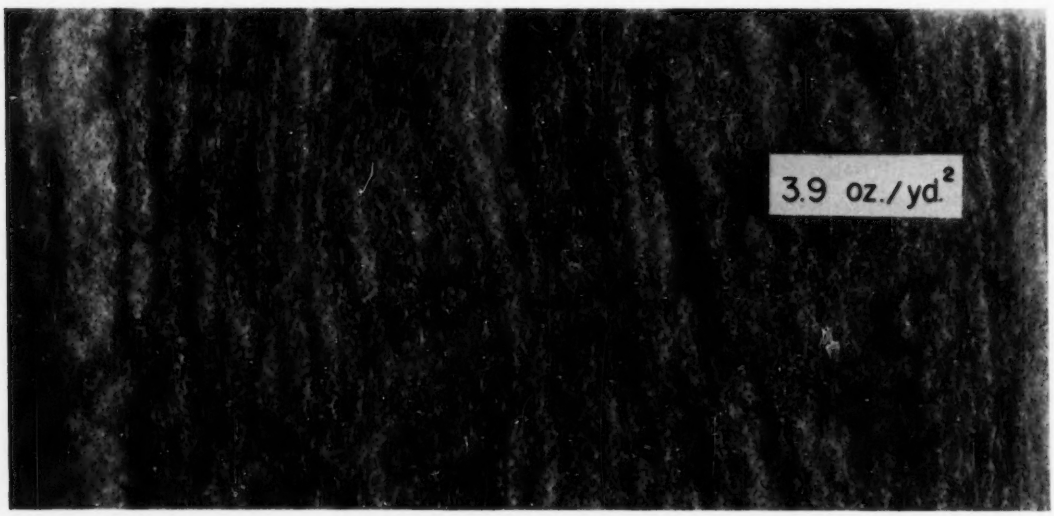
* This paper, issued as Quartermaster Textile Series Report No. 70, was presented in part at a meeting of Committee D-13 on Textiles of the American Society for Testing Materials in N. Y. C., Oct. 16, 1952. The work was sponsored by the Textile Section, Research and Development Branch, Office of The Quartermaster General.

achieved by cross-lapping the webs, the fibers remain essentially in a position normal with respect to the forces applied during actual use. In such a form the fibers behave in the manner of a beam—if the mechanics of fiber structure are compared with structural members. Since a beam is subject to greater deflection than a column of the same size and material, it is apparent that fibers in insulation fillers should be oriented, for optimum compression-resistance, in a direction parallel to the direction of applied compressive forces. The "snowfall" or random mat processes, for example, can be expected to allow, on the average, about one-third of the fibers to become oriented essentially in a direction along which axial compression dominates. Actually, such processes are employed commercially, and the orientation so attained has in some instances been retained effectively by fixing the structural configuration by means of elastomeric or resinous binders.

Under certain conditions—for instance, by the addition of heat-sensitive fibers—it is possible to achieve simultaneous random distribution, curling, and interlocking of fibers in a batting. Applying a heat treatment to these fibers causes them to shrink, curl, and bind to the other ingredients. Such preparations exhibit resiliency properties similar to those provided by randomly oriented and bonded fillers.

Finishing techniques are also applicable for improving insulation properties. Binders serve to retard fiber motion. The type of binder affects durability properties particularly when the finish is or becomes embrittled under conditions of service. Similarly, antilubricants, which also inhibit fiber motion, serve to maintain fiber structure and improve compressional resiliency.

None of the fibrous batt structures referred to, with or without improved fiber shapes or finishes, offer the type of improvement in insulation properties that are ultimately possible. More satisfactory fiber alignment for specific axial loading, however, is provided in pile constructions. Wool pile fabrics act as an effective insulation under low pressure, because the inherent resiliency of the wool gives a relatively high thickness. Under high pressure, however, the pile flattens. While this effect can be offset to a certain extent by not cutting the loops (as in the



Top View

End View

FIG. 1. *Very-low-density corrugated wool filler.*

frieze), the weight of the backing fabric and the pile yarns is responsible for a relatively high weight per unit area. Corrugated fibrous batts offer a possibility of achieving high resiliency with lower-weight materials.

Corrugated Fibrous Web Battings

In an attempt to overcome the deficiencies inherent in conventional fabrics, while retaining or even improving the advantages of the pile construction, the mechanics of fabric construction as applied to insulation properties were thoroughly studied. This work culminated in the development of the corrugated fibrous web type of insulation batting, a sample of which in very-low-density form is depicted in Figure 1. The process involves four important operations, two of which are commonly conducted in ordinary commercial practice: (*1*) The preparation of corrugated fibrous web batting employs first an orienting process of the card or garnet type. (*2*) The fibrous web so prepared is then buckled. The buckling action is conducted in such a manner that the web takes on the appearance of corrugations. These corrugations, for garment insulation applications, stand approximately ⅜–½ in. in height. (*3*) The next operation consists of a condensing technique, in which the buckled or corrugated web is "closed" to the desired density. (*4*) The last step in the process then involves a conventional quilting technique. Operation (*3*) can be accomplished by means of double-layer belt assemblies and is not unusual. Only the corrugating operation (*2*) introduces a new forming procedure. Corrugating processes have been applied commercially to various materials other than fibers, and the textile processors undoubtedly will develop for themselves a practical fiber forming practice. The methods used to prepare corrugated battings in this laboratory are presented below.

Pleating Techniques

The Laboratory Pleater.—The experimental, hand-operated pleating device used for preparing large-size samples is reproduced in Figure 2. The operation of this rather hastily constructed equipment is given as follows:

A web or lamination of webs to be corrugated is placed under the corrugating unit in such a manner that the end of the mat extends to the bar, *A*, which is free to move under the glass plate, *B*, and initially is positioned just under the edge of the glass plate. The eccentric, *C*, carrying the arm, *D*, and blade, *E*, is then turned in a clockwise rotation to move about ¾ in. length of the web toward the bar, *A*. The resistance to movements offered by the bar, *A*, causes the web to buckle and form the first pleat. Having thus formed the first pleat, it is then maintained between one of the metal straps, *F*, and the bar, *A*. The second pleat is formed in the same manner. Each complete turn of the crank causes the blade, *E*, to push forward about ¾ in., lift, and return to the initial point of contact. The second pleat, as the first, is maintained in position between the straps, *F*. After the third pleat is formed, the strap, *F*, nearest the bar, *A*, is removed, and the pleat that it held is main-

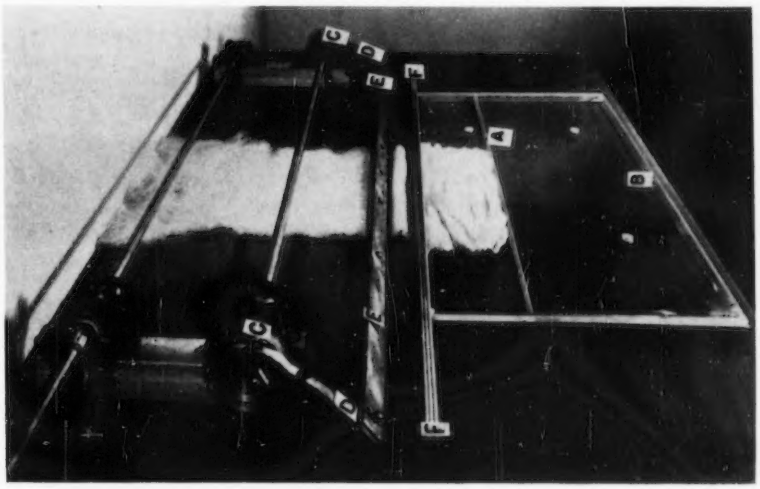


FIG. 2. *The laboratory pleater.*

tained between the bar, *A*, and successive pleats and the strap, *F;* the formed corrugated batting is retained under the glass plate. Thus, the processing continues, with each new pleat being held temporarily until moved under the plate, *B*, by a new pleat. The straps are repeatedly moved to hold each new and previous pleat in position.

The application of a water spray to the web prior to pleating or to the formed corrugated batting serves to soften natural fibers and facilitate the operation. During the drying operation, these fibers retain the shape in which they were positioned. Some semisynthetic fibers, particularly acetate rayon and regenerated cellulose, have also been successfully formed in this manner. When nylon is formed, a steam treatment with the temperature raised to a point exceeding the previous setting condition is necessary to effect retention of the corrugated construction. Softening and bonding, with the accompanying fixation of the corrugated structure, have been achieved through the use of a dilute aqueous dispersion of an elastomer or resin.

Several experimental corrugated fibrous web battings were prepared by the technique referred to above using four superimposed webs formed on a sample card. The four layers of web were employed in order that the number of corrugating operations could be reduced. This simplifying practice was required in order not to delay the evaluation program. Actually, it should be feasible to carry out the operation commercially on single webs and thereby obtain a batting of greater utility.

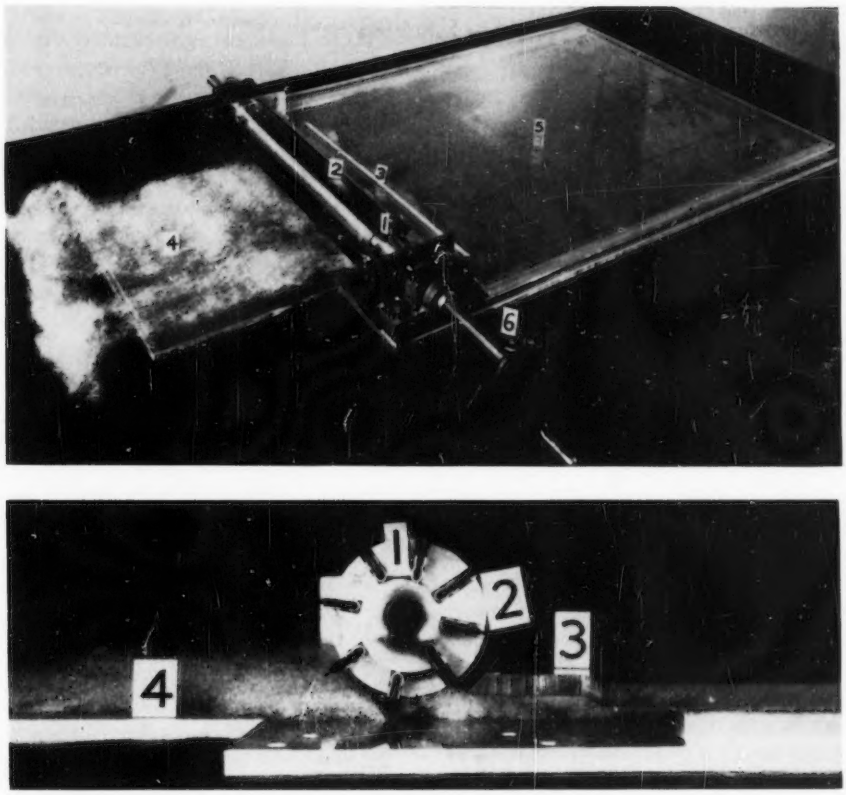
This laboratory corrugating unit was prepared and used to expedite the fabrication of samples for evaluation. It is not necessarily a pattern suggested for commercial corrugating, for the temporary features of the equipment introduced certain conditions which were not ideal for forming the best corrugated structure.

Commercial Pleating Machines. — Commercial pleating equipment is available for use on fabrics. Several varieties are manufactured and, with certain refinements and other modifications, they would seem to be applicable for corrugating fibrous webs. No use of the commercial pleaters for corrugating fibrous webs has been made so far, but the comments received from a representative of the Chandler Machine Company suggest confidence in the utility of such a device for rapidly corrugating a delicate fibrous web structure.

The Fibrous Web Crimper

The limiting features of the pleating operation— especially the apparent need for using paper over the web during commercial pleating and the difficulty of obtaining the card rate of speed— gave rise to the consideration of other corrugating methods. The most promising corrugating technique evolved from these studies has been the web crimper.

A laboratory model of the crimper is reproduced in Figure 3. It consists of a blade-roll assembly and base and top plates. As depicted, the blades in the blade-roll assembly are positioned in slots equidistantly located around the roll in such a manner that the blade (windshield wiper) tips touch the web at ¾-in. intervals. After each blade sweeps across the plate and forms a web as a corrugation, it recedes into the slot until it is flush with the roll surface. The corrugation is made by the moving blade and the resistance of the plain web to motion. The resistance is provided by the previously formed corrugated web, or initially by a bar placed on the first section of web passed through the crimper. Experiments also indicate that a canvas belt over the base plate or serving as a base plate offers sufficient resistance in itself to cause the web to buckle and form a corrugation. The position of the blade in the slot is controlled by the stationary cam pictured in the photograph as *1*. It will be noted that as the web, *4*, is received from the doffer of the carding machine, it is picked up by the blade, the blade making contact with and carrying the web as it sweeps across the plate. Since the roll turns in a counterclockwise direction, this blade continues to make contact with the web until it moves into the slot provided by the cam. At the point where the blade recedes into the slot, the formed corrugation passes under the top plate, *3*, where it is retained to offer resistance for forming succeeding corrugations, and where it slides freely between the plates by the force being applied as the result of the building up of such corrugations. The next blade then moves to the point of contact with the web and the operation is repeated. Since the distance between blades at the points of contact with the base plate is about ¾ in., each corrugation is ¾ in. in height. This distance also represents the spacing between the top and the base plate. For each revolution of the roll, 6 in. (8 in. × ¾in.) of web from the doffer is corrugated. Thus, with the web being provided at about 48 ft./min., the roll must be rotated at about 96 r.p.m.



End View

FIG. 3. *The fibrous web crimper.*

In practice, the equipment has operated exactly as indicated when carded cotton, nylon, or wool web was used as feed. Ordinarily, however, particularly at speeds approaching 96 r.p.m., the fibers tend to adhere sufficiently to the blades and/or slot to cause the formed web to pass through the space between the top plate and the roller. Not until the top plate was vibrated could this difficulty be avoided. With one end stationary, the end nearest the roll was vibrated through an arc of about ¼ in. It seems that the difficulty might also be avoided through the use of canvas belts—one placed immediately over the base plate and the other above this, and separated by the thickness (⅜ in.) of the formed batt. Since these belts travel at just sufficient speed to permit suitable web crimping without allowing the formed corrugation to condense significantly just after forming, they should prevent the formed web from riding over the roll in the manner described above. The treating of the corrugated web may be carried out just beyond this first belt assembly in a section of separated plates, while the condensing of the formed and/or treated web can be accomplished by another set of double-layer conveyer belts.

This principle of forming corrugated web appears, from limited observations, to be quite sound. Further development, however, is needed to carry the operation to a point of commercial usefulness.

Carding Corrugating

Another corrugating process involving the use of the card alone has been considered. This method of corrugating fibrous webs may be more readily adaptable to commercial operation than those techniques previously described, particularly when relatively thick (1.5 in.) battings are desired. The

technique requires that the speed of the take-off apron of the carding machine be reduced to permit the doffer comb to build up the web in the form of corrugations. In the ordinary operation of a carding machine, the periodic motion of the combs produces the corrugations, but the sweep of the comb is relatively great and the webs are straightened or even stretched as a result of the excessive take-off apron speed. By means of relatively minor modifications, it may be possible to carry out the entire course of operations required for forming corrugated fibrous battings directly on the carding or garnetting equipment.

Variations in Composition and Structure of Corrugated Battings

Fiber Treatment.—In preparing corrugated battings it is usually advantageous or even necessary to apply a finish to the fibrous web. Softening of the fiber facilitates the shaping of the web, and frequently the treatment may actually serve to fix the corrugated structure. Resinous and elastomeric dispersions as well as water and steam have been used to this end in preparing corrugated fibrous fillers. The moistening or steaming of most natural fibers provides a condition for temporarily setting the structure. The steam-pressure treatment of nylon and of certain other thermoplastic fibers is effective in holding and maintaining the batt structure until more severe conditions of exposure are encountered. Resinous and elastomeric finishes applied to either natural or synthetic fibers perform as a fixative, a binder, or both.

Fiber Additives.—It is evident that coarse, stiff, crimped fibers impart good compression-resistance. The inclusion of fine fibers, however, causes the area of contact between individual fibers to be lessened and increases the resistance to heat flow. In the corrugated form, similarly, fiber properties are instrumental in determining filler characteristics. However, in the new forming process it is possible to add to a web of the preferred size and type of fibers coarse, stiff, uncrimped filaments in their continuous form, and thereby achieve all the advantages of the stiff fiber. Preferably, the stiffening fibers are included in a corrugated filler by spacing continuous monofilaments across, superimposed on, and in the same direction as the web of selected fibers just prior to the buckling operation. The greater stiffness of the added filaments, together with their method of orientation in the corrugated form, provides a batting of unusual compression-resistance and accompanying high over-all insulation efficiency.

Wave Pattern and Durability.—Before corrugated fibrous web battings were evaluated for simulated wear-resistance, concern was expressed about the possible separation of the pleats during use. In an effort to inhibit degradation of this nature, the additional application of a wave pattern on the finished corrugated filler was considered. The effectiveness of the wave pattern in reducing pleat separation is based on mechanical principles wherein the forces applied transversely to the waved corrugated structure are counteracted by the greater resistance to movement offered by this arrangement of the pleated fibrous webs. Presumably, similar advantages can be achieved by performing the quilting operation at an angle of about 45° rather than 90° to the direction of the ridges in a straight corrugated batting. Actually, however, experimental straight corrugated interliners (quilted in a 5-in. box pattern between nylon facing fabrics) have displayed no significant separation after 20,000 cycles of flexing on the simulated wear tester. Their behavior in actual use in clothing is still to be determined.

Properties of Corrugated Fibrous Web Fillers

The properties of experimental corrugated fibrous web fillers have been compared in laboratory testing with conventional laminated and pile fabrics. Inasmuch as low density is of primary importance, the corrugated samples have usually been prepared at about 1 oz./ft.² (before quilting). This is the weight of some laminated and randomly oriented fiber fillers

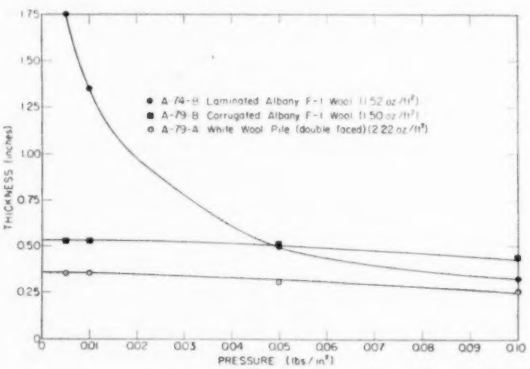


FIG. 4. *Influence of batt structure on compression-resistance of wool (nonquilted battings).*

that have been considered for use in military equipage, and is lower than that for wool pile. Comparison of the over-all insulation properties of these pile fabrics with the lightweight corrugated battings formed from the same fibers as woven fabrics is favorable to the corrugated material.

In an examination of about 150 experimental and commercial insulation fillers for over-all insulation properties, the laboratory corrugated samples were shown to be the most efficient. The corrugated structure provides high resistance to compression at low density, and also shows thermal conductivity properties which are no greater and may be even less than those found for fillers prepared in the conventional pile or laminated web structure. Furthermore, these advantages for the new fill construction are maintained after simulated wear testing.

The compression-resistance properties of laminated web, corrugated web, and pile battings prepared from wool fibers are compared in Figure 4. Both the laminated web and corrugated web fillers were formed at approximately the same density in the laboratory from an F-1 grade wool supplied by the Albany Felt Company. The laminated wool batting, naturally, is quite thick under low pressure, but both the corrugated and pile preparations are far superior in retaining their thickness as the applied pressure is increased. Actually, the corrugated web sample is the thickest under 0.05 lb./in.^{2} pressure, even though the pile fabric is almost 50% heavier. Since the quilting operation reduces the initial thickness of loose fillers, the initial advantage in thickness displayed by the laminated web battings is not a factor when the batting is fabricated as a garment interliner.

In Figure 5, the effect of somewhat higher compressive loads on the thickness of quilted laminated webs and corrugated webs is shown. The corrugated wool batting (B-1) is superior in compression-resistance, even after having been subjected to 5,000 cycles of flexing, to the conventional type filler before the flex treatment. These same differences are displayed graphically in Figure 6, which compares the compressional properties of the following cotton battings: laminates of garnetted web, random mat, and corrugated random mat. These curves again indicate the superiority of the corrugated structure, and it is particularly noteworthy that the simulated wear test again has the least destructive influence on the new form of insulation filler.

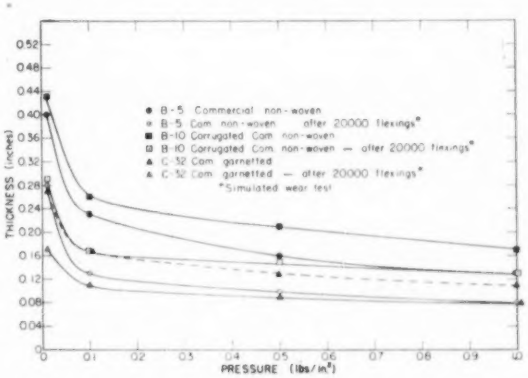

B-5 Commercial non-woven
B-5 Com. non-woven after 20000 flexings*
B-10 Corrugated Com. non-woven
B-10 Corrugated Com. non-woven — after 20000 flexings*
C-32 Com. garnetted
C-32 Com. garnetted — after 20000 flexings*
*Simulated wear test
THICKNESS (inches)
PRESSURE (lbs/in²)

FIG. 6. *Comparative compression-resistance of quilted cotton battings (approximately equal densities of 1.7 oz./ft.^{2}).*

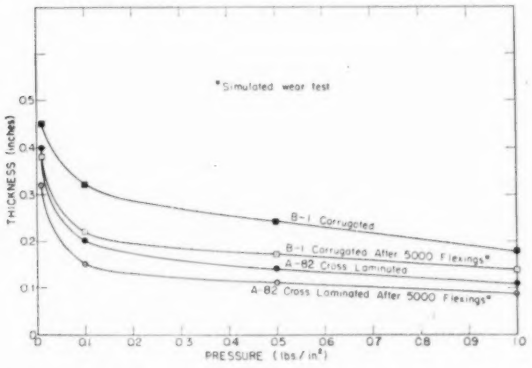


FIG. 5. *Influence of batt structure on compression-resistance of wool (Harriset, 50's) (quilted battings, approximately 1.5 oz./ft.^{2}).*

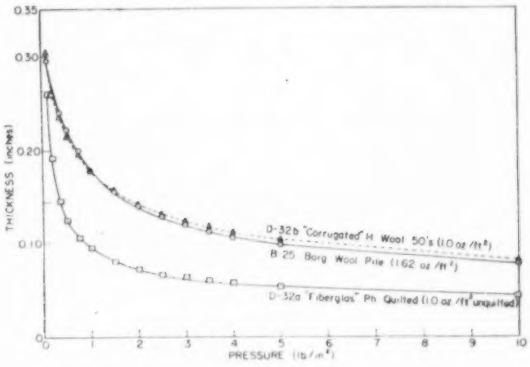

D-32b "Corrugated" H. Wool 50's (1.0 oz./ft²)
B-25 Borg Wool Pile (1.62 oz./ft²)
D-32a "Fiberglas" Ph. Quilted (1.0 oz./ft² unquilted)
THICKNESS (inches)
PRESSURE (lb./in²)

FIG. 7. *Compression-resistance: standard vs. experimental battings.*

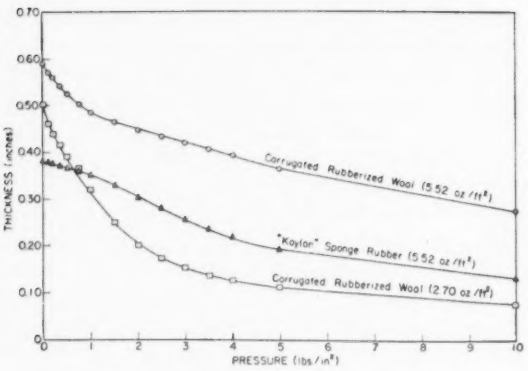


FIG. 8. *Compression-resistance: sponge rubber vs. corrugated rubberized wool.*

The compression-resistance properties, over a range of relatively high pressures, for a corrugated wool, a low-density pile fabric, and a fibrous glass filler are compared in Figure 7. Throughout the range of loading (above 1 lb. pressure), the corrugated sample is at least twice as thick as the fibrous glass batting. Furthermore, in spite of its higher density, the pile fabric performs little or no better, compressionwise, than the corrugated web preparation.

The comparative cushioning properties of corrugated rubberized wool and a commercial foamed rubber are given in Figure 8. A shoddy wool was used in preparing each of the corrugated samples, and the rubber add-on amounted to 20% on a weight basis. The elastomer employed in this instance served only to fix the fibers in the web prior to forming, and did not bond together the pleats in the improved insulation structure. These curves again indicate that for equivalent weights the corrugated structure is superior to the uncorrugated sponge rubber.

The foregoing results clearly demonstrate the superior compression-resistance of the experimental corrugated web structures. These findings are important only if thickness and insulation efficiency are directly proportional. Insulation efficiency may be expressed as being equivalent directly to thickness and inversely to the coefficient of thermal conductivity and density. With the density of the battings maintained at a constant value, and the improved thickness properties of corrugated battings demonstrated, only the influence of structure on thermal conductivity remains to be considered. In none of the experimental corrugated fibrous web battings has the coefficient of thermal conductivity been found to be greater than that determined for conventional laminated web battings of the same fiber. In fact, as is indicated in Table I, the relative coefficient of thermal conductivity for corrugated web battings is equal to or less than that value determined on other forms of fibrous insulation fillers of the same ingredients.

TABLE I. EFFECT OF BATT FORM* ON THERMAL CONDUCTIVITY†

Interliner	Relative thermal conductivity coefficient $K = \frac{\text{B.t.u.}}{\text{hr., °F, ft.}^2\text{/in. thickness}}$
Wool, Albany felt F-1, corrugated	0.35
White wool pile, double-faced	0.37
Harriset wool (50's), corrugated	0.39
Harriset wool (50's), plus elastomer, corrugated	0.41
Harriset wool (50's), cross-laminated	0.41
Wool, Albany felt F-1, cross-laminated	0.42

* Battings were subjected to 5,000 cycles of flexing.
† The loading pressure was .01 lb./in.².

TABLE II. LAUNDERING TESTS

Sample No.	Composition-construction	Shrinkage (%) after 3 launderings Warp	Fill
A-82	Harriset wool 50's (laminated carded webs)	13.3	16.7
B-1	Harriset wool 50's (corrugated carded webs)	3.3	8.3
C-31	White wool pile (woven)	7.2	8.3
B-25	"Borg" wool pile nylon back (knitted)	6.3	6.7

The results of laundering tests (Table II) also indicate that corrugated fillers perform better or no less satisfactorily than ordinary insulation materials. The shrinkage (decrease in width and length) of various experimental and commercial fillers after three mobile launderings is given.

Conclusions

In the laboratory, experimentally formed corrugated fibrous web fillers have displayed outstanding compressional resiliency properties. When formed in this manner, any fiber may be expected to provide a level of compression-resistance which is superior to

that offered by the same fiber in conventional form. Abrasion properties are not adversely affected, and thermal conductivity characteristics may actually be improved by this fiber orientation process. As a result, the over-all insulation properties of corrugated fibrous web fillers are maintained at a level which appears to be optimum for the fiber used.

The corrugating operation should not be difficult to adapt to commercial practice. Potentially, the process offers a means of producing improved insulation fillers in quantity and on conventional equipment with relatively minor modifications and/or attachments.

All these facts considered, it is suggested that the corrugating technique, which presents a possibility of converting less satisfactory fibers into an improved insulation filler, be seriously investigated by the American textile industry as a commercial method for preparing fibrous fillers.

Acknowledgment

The assistance of Mr. Norris Barbre and Mr. Henry A. Sinski, formerly of the Quartermaster Textile Materials Engineering Laboratory, is gratefully acknowledged. Acknowledgment is made to Mr. Gerald Winston and Mr. John Medernach for the preparation of the graphical material, and to Dr. Oscar Mandel for editorial assistance. Appreciation is also expressed to Dr. S. J. Kennedy, Research Director for Textiles, Clothing and Footwear, Office of The Quartermaster General, for his support of this work and for permission to publish this paper.

(Manuscript received October 22, 1952.)

Silicon-Containing Azo Dyes
Part IV: Dyeing Properties and Lightfastness *

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Abstract

The dyeing properties and the lightfastness on cellulose acetate rayon of several azo dyes prepared from *m*-trimethylsilyl- and *m*-triphenylsilyl-*N,N-bis*-(β-hydroxyethyl)-aniline have been examined.

The dyes derived from *m*-triphenylsilyl-*N,N-bis*-(β-hydroxyethyl)-aniline have been found to lack substantivity for cellulose acetate and to have inferior lightfastness, whereas the dyes obtained from the trimethylsilyl analogue showed fairly good substantivity and very good lightfastness. A comparison of the dyeings and the lightfastness of some of the dyes synthesized from *m*-trimethylsilyl-*N,N-bis*-(β-hydroxyethyl)-aniline with those of the corresponding dyes obtained from the methyl analogue, which are commercial dyes, has revealed that the substantivity of the silicon-containing azo dyes is less, but the lightfastness is more, than those of the commercial azo dyes.

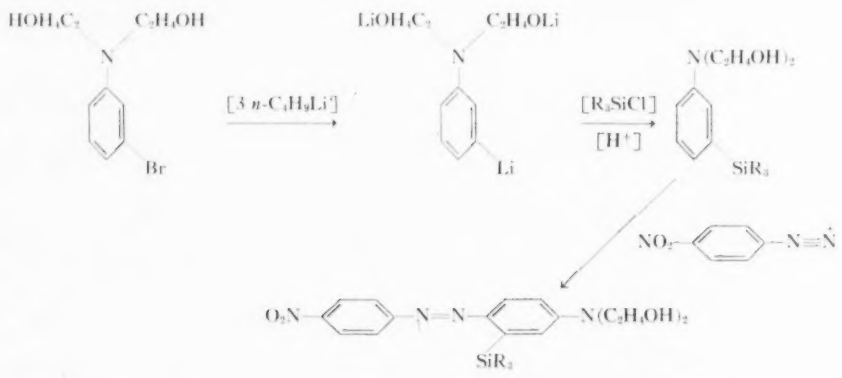
The reflectance spectra of the 1% shades of some of the azo dyes have been recorded, and the Munsell renotations for hue, lightness, and chroma of the color of the dyes have been determined.

In a previous publication [7] the present authors reported the dyeing properties and the lightfastness of some azo dyes prepared from *m*-trimethylsilyl- and *m*-triphenylsilyldimethylaniline. However, since these dyes lacked the desirable affinity and lightfastness required for a comparative study, we believed it necessary to prepare more new silicon-containing azo dyes, related to some commercial types, derived from *m*-trimethylsilyl- and *m*-triphenylsilyl-*N,N-bis*(β-hydroxyethyl)-aniline. The synthesis and properties of these dyes have been reported elsewhere [6]; reported herein are their dyeing and lightfastness properties on cellulose acetate rayon.

* Part I appeared in *The Journal of Organic Chemistry* **15**, 1200 (1950); Part II will appear in *The Journal of Organic Chemistry;* and Part III appeared in TEXTILE RESEARCH JOURNAL **22**, 574 (1952).

The lack of substantivity of most of the common dyes for cellulose acetate has limited the field of suitable dyes for this fiber to the dyes which are basic in character—especially azo, aminoanthraquinone, nitroarylamine, and methine. Furthermore, since in the dyeing process the dye is reported to dissolve in this fiber, the molecular weight of the dye is an important factor in determining its substantivity [8]. Therefore, in the case of azo dyes the desirable changes in hue, brightness, and fastness have been effected mainly by the appropriate substituents in the parent azo dye, 4-aminoazobenzene. Both *N*-alkylation and nuclear substitution have been found to facilitate these changes [3, 5]. Among the different *N*-alkylated amines used as coupling components, *N,N-bis-*(β-hydroxyethyl)-*m*-toluidine is of particular importance. Therefore, *m*-trimethylsilyl- and *m*-triphenylsilyl-*N,N-bis-*(β-hydroxyethyl)-aniline were the compounds preferred for the present investigation [6].

The organosilicon compounds were prepared by the reaction of trimethylchlorosilane or triphenylchlorosilane with the organolithium compound, prepared by the reaction of *n*-butyllithium with *m*-bromo-*N,N-bis-*(β-hydroxyethyl)-aniline [6]. The azo dyes were synthesized by coupling selected diazonium



salts with the above two silicon compounds in acetic acid solution. The resulting dyes were carefully purified and used for the dye trials.

Discussion

The dyes derived from *m*-trimethylsilyl-*N,N-bis-*(β-hydroxyethyl)-aniline and *m*-triphenylsilyl-*N,N-bis-*(β-hydroxyethyl)-aniline showed a considerable difference in their dyeing properties. The most striking difference was that dyes prepared from the latter compound showed a very poor substantivity, whereas those obtained from the former possessed fairly good substantivity for cellulose acetate fabrics. A similar difference was noted in their lightfastness. The triphenylsilyl derivatives had lightfastness of 20 hrs., whereas in the case of the trimethylsilyl derivatives the lightfastness varied from 50 to 60 hrs., which is supposed to be very good in comparison with that of the dyes currently used. Similar differences in the shades and lightfastness of the dyes derived from *m*-trimethylsilyldimethylaniline and *m*-triphenylsilyldimethylaniline have already been noted [7]. For the reason stated previously, the general lack of substantivity of dyes I to V may be attributed to the bulkiness of the triphenylsilyl group.

A close comparison of dyes VI to VIII (Table I) with similar commercial dyes—such as Celliton Red GG [*p*-nitroaniline → *N,N-bis-*(β-hydroxyethyl)-*m*-toluidine], Celliton Fast Rubine 3B [2-chloro-4-nitroaniline → *N,N-bis-*(β-hydroxyethyl)-*m*-toluidine], and Celliton Fast Brown 5R [2,6-dichloro-4-nitroaniline → *N,N-bis-*(β-hydroxyethyl)-*m*-toluidine]—reveals some minute differences. The 0.083% shades of dyes VI and VII are almost the same as those of the first two commercial dyes in both hue and brightness. However, in the heavier shades (1%) there is a notable difference in the hue of the shades. For example, the 1% shade of dye VI is more yellow than the corresponding shade of Celliton Red GG, and the 1% shade of dye VII is less purple than the corresponding shade of Celliton Fast Rubine 3B. This slight change in the hue in 1% shades may be due to the decrease in the substantivity of dyes VI and VII, because the weaker shades of the

same dye when compared with its slightly heavier shades indicate an hypsochromic effect. A marked difference was noted in the shades of dye VIII and those of the corresponding methyl analogue, Celliton Fast Brown 5R. The latter gives shades of red-brown color, whereas dye VIII gave yellow-brown shades similar to those of Celliton Brown 3R [2,6-dichloro-4-nitroaniline → *N,N*-β-hydroxyethylmethylaniline].

The lightfastness of all the dyes (VI–XI) is quite satisfactory. In the lighter shades the fastness is generally about 40 hrs., and in the heavier shades the fastness is as much as 60 hrs. A comparison of the lightfastness values of dyes VI, VII, and VIII with those of the corresponding commercial dyes indicates that the trimethylsilyl group slightly increases the lightfastness, the difference being more noticeable in the lighter shades (0.083%). For example, there is definite fading in the 0.083% shades of dyes VI to VIII after an exposure of 40 hrs., whereas the commercial dyes indicate a distinct fading after 20 hrs. exposure. In the heavier shades (1%), all of them with the exception of Celliton Fast Brown 5R show a fastness of 60 hrs. In the case of Celliton Fast Brown 5R, the fastness is only 40 hrs., but the fastness of dye VIII in 1% shade is about 60 hrs. Thus, in this pair the trimethylsilyl group shows a definite improvement over the methyl group in both the hue and the lightfastness of the shades.

Next, by comparing the Munsell renotations of the

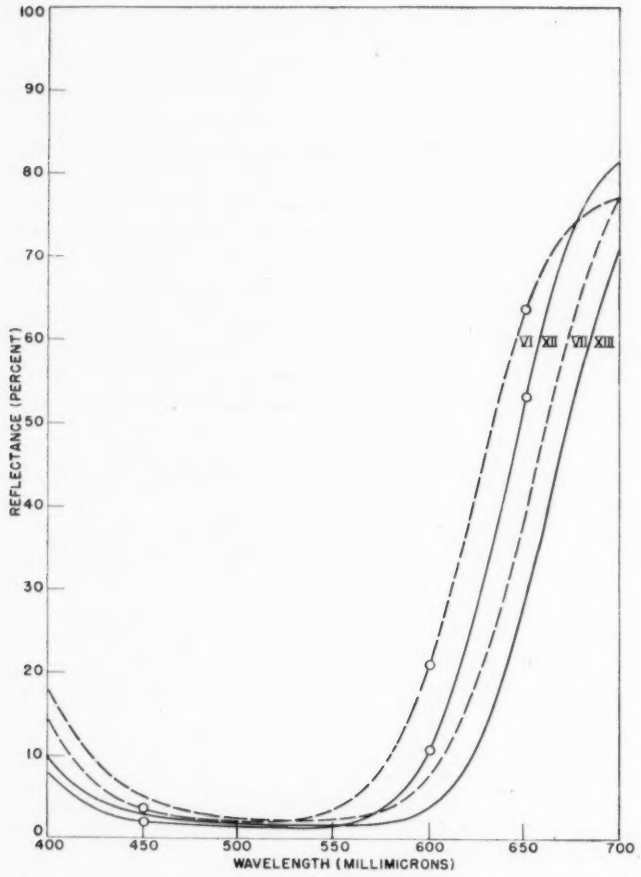
TABLE I. DYEING PROPERTIES AND LIGHTFASTNESS OF SILICON-CONTAINING AZO DYES

Dye No.	Diazo component, aniline derivative	Color of the dye	0.083% Shade on Estron: Color and tone of shade*	0.083% Shade on Estron: Light-fastness (hrs.)	1% Shade on Estron: Color and tone of shade*	1% Shade on Estron: Light-fastness (hrs.)	Munsell renotations†
			Coupler: m-*Triphenylsilyl*-N,N-bis-(β-*hydroxyethyl*)-*aniline*				
I	4-Nitro-	Brown-red	Flesh Pink d	20	Baby Pink d	20	—
II	2-Chloro-4-nitro-	Bordeaux	—	—	Orchid d	20	—
III	2,6-Dichloro-4-nitro-	Brown-red	Not tested	—	—	—	—
IV	2-Methylsulfonyl-4-nitro-	Blue-violet	Lavender d	20	Lavender d	20	—
V	2,4-bis-(methylsulfonyl)-	Dark red	Baby Pink d	20	Arbutus Pink d	20	—
			Coupler: m-*Trimethylsilyl*-N,N-bis-(β-*hydroxyethyl*)-*aniline*				
VI	4-Nitro-	Brown-red	Geranium m	20–40†	Scarlet b	40⁺	5.5⁺R 3.72/12.4
VII	2-Chloro-4-nitro-	Blue-violet	Violine Pink m	40⁺	Magenta b	60	0.5R 2.53/9.9
VIII	2,6-Dichloro-4-nitro-	Brown-red	Honeydew m	40	Burnt Orange b	60	2YR 5.05/9.1
IX	2-Trifluoromethyl-4-nitro-	Blue-violet	Violine Pink m	40⁺	Red Grape b	60⁺	5⁺RP 2.79/9.7
X	2-Methylsulfonyl-4-nitro-	Blue-violet	Amethyst m	40⁺	Dahlia Purple b	60⁺	0.5⁻RP 2.41/10.2
XI	2,4-bis-(methylsulfonyl)-	Brown-red	Peach Blossom m	40	Geranium b	60⁺	2.5R 5.08/11.7
			Commercial dyes				
XII	Celliton Red GG	—	Geranium m	40	Cardinal b	40⁺	6⁺R 2.86/11.5
XIII	Celliton Fast Rubine 3B	—	Violine Pink m	20⁺	Garnet b	60	8.5⁻RP 1.79/8.6
XIV	Celliton Fast Brown 5R	—	Grecian Rose m	20⁺	Lacquer m	40	7.5R 3.77/8.2

* Tone of the shades: b = bright; m = medium; d = dull.

The names of the color of the shades were given after matching the shades, as closely as possible, with those in the "Standard Color Card of America," 9th ed., created and issued by The Textile Color Card Association of the United States, Inc., 1941.

† Superscripts ⁺ and ⁻ indicate slightly more and slightly less than the number concerned, respectively.



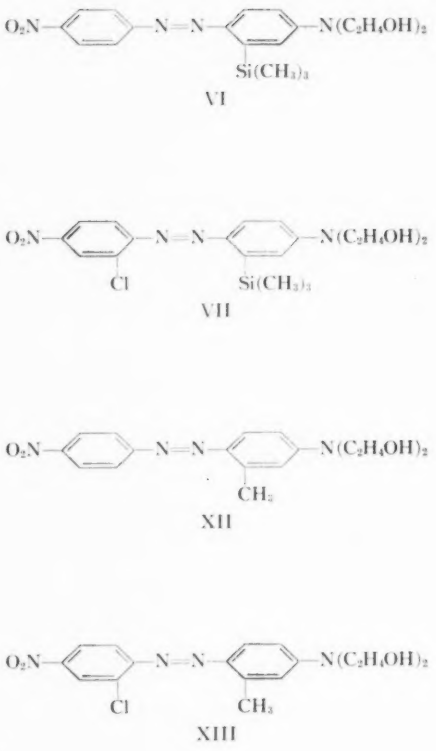
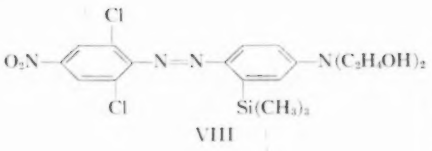
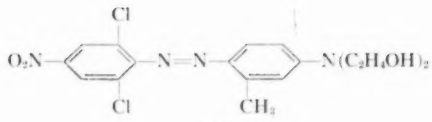


FIG. 1. *Spectral reflection curves of cellulose acetate fabrics dyed (1%) with dyes Nos. VI, VII, XII, and XIII (Table I).*

color of the shades, the minute differences in the hue, lightness, and chroma of the dyes can be noticed. The Munsell hues for dyes VI, VII, and VIII are 5.5°R, 0.5R, and 2YR, respectively; and for the corresponding commercial dyes, 6°R, 8.5°RP, and 7.5R, respectively. This indicates that the color of dye VI is more red, that of dye VII is less purple, and that of dye VIII is much more yellow than the color of the corresponding commercial dyes. Thus, in general, the trimethylsilyl group seems to have an hypsochromic effect on the color. In this connection, it may be mentioned that even though the Munsell hue for dye VI indicates more red in the color than that for the corresponding commercial dye, the actual shade of dye VI looks more yellow-red than that of Celliton Red GG. Both the lightness and chroma of dyes VI, VII, and VIII are greater than those of the commercial dyes. The curves in Figures 1 and 2 also indicate that dyes VI–VIII reflect more light than the corresponding commercial dyes. The reflectance (%) of the light by a dye on the fiber depends upon both its absorption of the light and the percentage of the dye on the fiber. Therefore, since the absorption of light by the silicon-containing azo dyes and also by the corresponding dimethylaniline analogues is almost the same [7], the higher reflectance (%) for dyes VI–VIII than for the corresponding commercial dyes indicates that in the latter case the percentage of dye on the fiber is greater, or, in other words, the substantivity of the commercial dyes



VIII



XIV

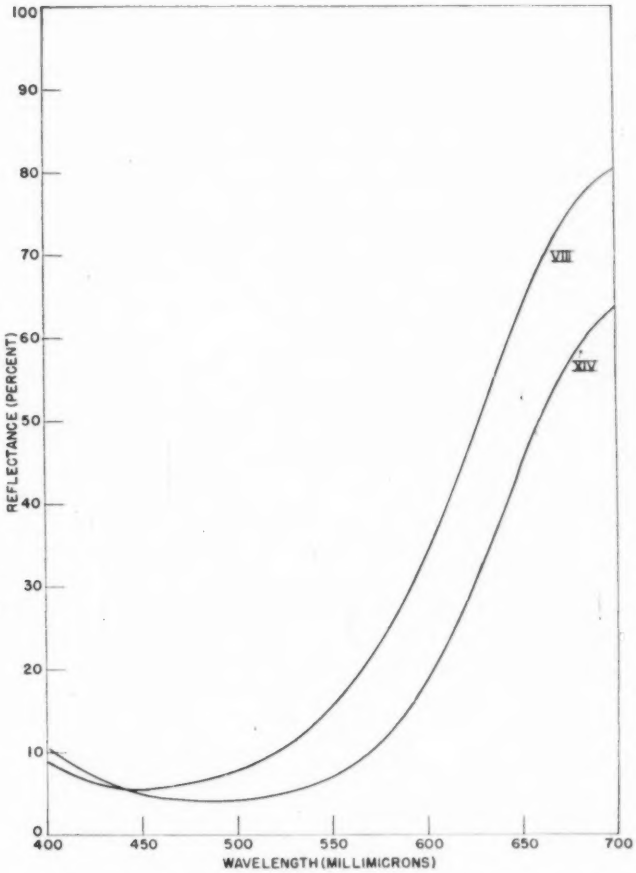


FIG. 2. *Spectral reflection curves of cellulose acetate fabrics dyed (1%) with dyes Nos. VIII and XIV (Table I).*

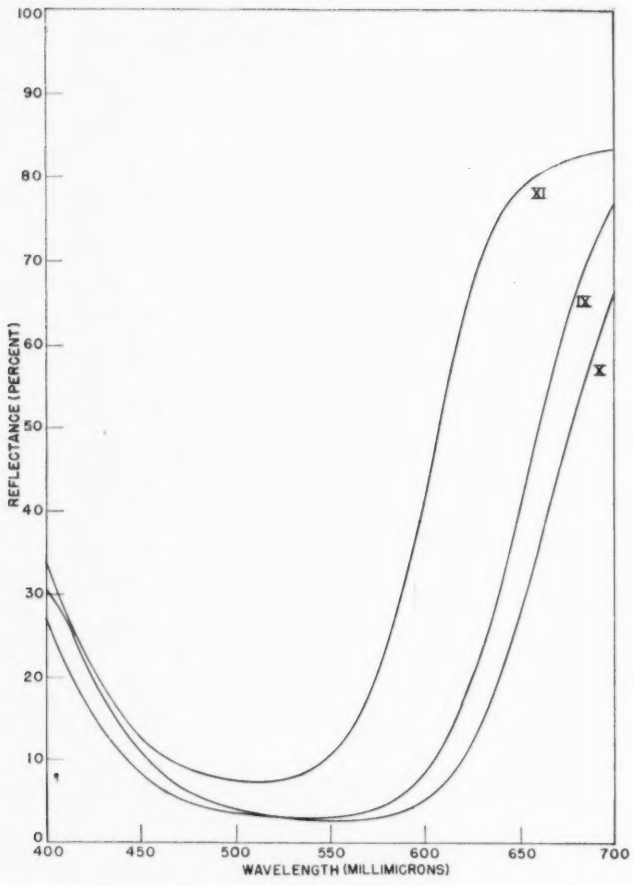
is more, than that of the corresponding silicon-containing azo dyes.

Experimental

The silicon-containing azo dyes were prepared by a standard procedure by coupling the diazonium salts with the silicon compounds in acetic acid solution [6]. The resulting dyes were purified by chromatographic fractionations followed by crystallization from appropriate solvents. Pure dyes were used to test their shades on cellulose acetate fabrics by a standard dyeing procedure [7]. For comparison, commercial dyes—Celliton Red GG, Fast Rubine 3B, and Fast Brown 5R—were used for dyeing 0.083% and 1% shades (based on 100% purity of the dyes). The cloth used for the dye tests was a 100% acetate, dull-luster, knit jersey fabric.

The lightfastness was determined on a standard fadeometer, and 1 hr. exposure to the fadeometer was thought to equal 1 hr. exposure to the summer sun at high noon. Details of the dyeing properties and lightfastness are reported in Table I.

The reflectance curves of the shades were obtained on a General Electric Recording Spectrophotometer, using magnesium oxide as a white standard for comparison. Computations of tristimulus values were made automatically by the GAF-Librascope Tristimulus Integrator while the spectral reflection curves were being run [1]. Conversion of X, Y, and Z to "value" unit V_x, V_y, and V_z was done by using the



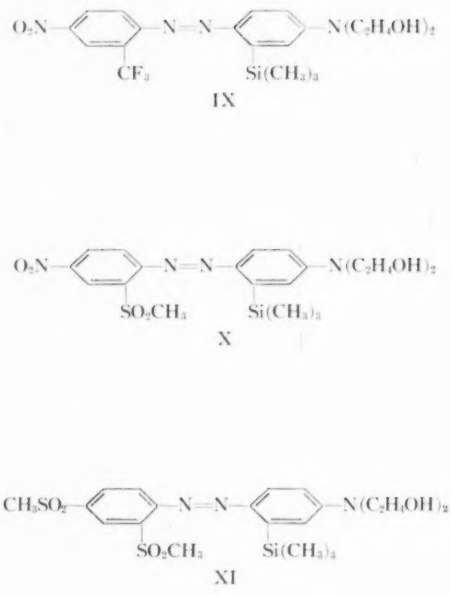


FIG. 3. *Spectral reflection curves of cellulose acetate fabrics dyed (1%) with dyes Nos. IX, X, and XI (Table I).*

Nickerson [4] tables, and the Munsell hue and chroma for the color were found from the chromaticity diagrams [2]. The reflectance curves are given in Figures 1 to 3.

Acknowledgment

The authors wish to thank Dr. I. H. Godlove of General Aniline and Film Corporation for his aid in the spectrophotometric work, and Mr. Howard Hartzfeld of this Department for his cordial assistance. They are particularly grateful to Dr. J. B. Dickey of the Tennessee Eastman Company for his very valuable suggestions and assistance.

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(Manuscript received October 1, 1952.)

Further Studies on the Method of Determining the Concentration Dependence of the Diffusion Coefficient

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Introduction

In a previous paper [5] the authors presented a method of determining the concentration dependence of the diffusion coefficient from experimental sorption data on the basis of the method of moments as applied to diffusion problems [3]. Although for the data obtained by Prager [7] with a polyisobutylene-isobutane system the method was found to give results which agreed satisfactorily with Prager's calculations by a different method, the diffusion coefficient obtained increases only by a factor of about 10 over the concentration range examined. In addition, the purpose of the calculation was substantially to check the validity of the method and not to determine a new concentration dependence from given sorption data. For the latter purpose, it is necessary to carry out the procedure described in the previous paper by assuming an appropriate polynomial representation for the diffusion coefficient in question. It may be performed without great difficulty if three or less coefficients in the polynomial suffice to determine the result of desired accuracy. By increasing the number of assumed coefficients, the calculations involved become excessively increased, and the method actually ceases to be applicable. Such a difficulty was experienced by us when the method was applied to the experimental data obtained by Crank and Park [2] for the system polystyrene-chloroform. For this reason, it was desired to modify the method so as not to assume the polynomial approximation in the analysis. An effort has been made in this direction, and the results obtained are presented in the present paper. It was found that, with some modification, the algebraic procedure in the previous method can be replaced by a graphical integration of a certain simple nonlinear differential equation of the first order, and the method thus becomes much simplified so that it can be applied in a straightforward manner to any given sorption data.

The Modified Method

It is convenient to repeat the statement of the problem and the relevant equations as set forth in the previous paper [5]. Suppose that an infinite sheet of uniform material of thickness l is placed in a solution, and that the solute is allowed to diffuse into the sheet. It has been shown both experimentally and theoretically that when the surface concentration of the solute is maintained at a constant value (say, C_o) throughout the process, and if the film resistance to material transfer at the surface of the sheet may be neglected, Q_t, the amount of sorbed solute per unit area of the sheet at time t can be represented by the equation

$$Q_t = 2K(C_o)\sqrt{t} \tag{1}$$

for values of t in which the sheet behaves as a semi-infinite medium. According to a recent paper by Crank [1], however, equation (1) may be applied somewhat beyond the time at which the concentration at the mid-section of the sheet ceases to be effectively zero. In equation (1), $K(C_o)$ is a function of C_o only, the form of which can be obtained from sorption experiments carried out at different concentrations of the external solution. The purpose of the present paper is to give an approximate method for determining the form of the diffusion coefficient from this experimental information on $K(C_o)$.

As shown in the previous paper [5], according to the method of moments [3], which recently has been used rather extensively by one of us in connection with approximate solutions of various problems in concentration-dependent diffusion, $K(C_o)$ may be represented approximately by

$$K(C_o) = \sqrt{D(0)}\, C_o \left(\frac{1}{8\sqrt{\beta}} + \frac{1}{12}\alpha\sqrt{\beta} \right), \tag{2}$$

where

$$\alpha = \frac{30}{C_o}\int_0^{C_o} \frac{D(C)}{D(0)}\, dC, \tag{3}$$

and β is a larger positive root of the quadratic equation

$$\left[720\frac{D(C_o)}{C_oD(0)}\int_0^{C_o}\frac{D(C)}{D(0)}dC\right]\beta^2 + \left[\frac{30}{C_o}\int_0^{C_o}\frac{D(C)}{D(0)}dC - 108\frac{D(C_o)}{D(0)}\right]\beta + \frac{3}{2} = 0. \quad (4)$$

$D(C)$ is the value of the diffusion coefficient at a concentration C.

Introducing the new quantities $f(C)$ and $g(C)$, defined by

$$f(C) = \frac{D(C)}{D(0)} \quad (5)$$

$$g(C) = \frac{1}{C}\int_0^C \frac{D(C)}{D(0)}dC, \quad (6)$$

equation (4) is written

$$720f(C_o)g(C_o)\beta^2 + [30g(C_o) - 108f(C_o)]\beta + \frac{3}{2} = 0,$$

which, on defining x and y by

$$x = \beta g(C_o) \quad (7)$$

$$y = \frac{g(C_o)}{f(C_o)}, \quad (8)$$

is reduced to the form

$$720x^2 + (30y - 108)x + \frac{3}{2}y = 0. \quad (9)$$

If we solve this equation for x and take into account that the larger positive root fits our requirement, we obtain

$$x = \frac{(54 - 15y)}{720}\left\{1 + \left[1 - \frac{1080y}{(54 - 15y)^2}\right]^{\frac{1}{2}}\right\}. \quad (10)$$

Let us now introduce a limitation for $D(C)$, to be considered below. In what follows, we shall be interested only in $D(C)$ which increases monotonously with increasing C. It is then readily shown that for such a $D(C)$ the following condition holds:

$$0 < y < 1. \quad (11)$$

With this condition in mind, the right-hand side of equation (10) may be expanded in powers of y to give

$$x = \frac{3}{20}\left[1 - \frac{10}{27}y - \frac{25}{729}y^2 + O(y^3)\right], \quad (12)$$

where O is a symbol signifying the order of magnitude. On the other hand, from equation (2) we have

$$64\frac{F(C_o)}{g(C_o)}x = (1 + 20x)^2, \quad (13)$$

where

$$F(C_o) = \frac{[K(C_o)]^2}{D(0)C_o^2}. \quad (14)$$

Substituting for x from equation (12) and arranging the resultant equation in a series of y, there results

$$\frac{3}{5}\frac{F(C_o)}{g(C_o)} = 1 - \frac{5}{27}y - \frac{175}{2916}y^2 + O(y^3). \quad (15)$$

Provided that the terms higher than $O(y^2)$ may be neglected in comparison with unity, equation (15) may be rewritten

$$f(C_o) = \frac{\frac{5}{27}g(C_o)}{1 - \frac{3}{5}\frac{F(C_o)}{g(C_o)}}, \quad (16)$$

where equation (8) has been taken into account. From equations (5) and (6) the following relation can be obtained:

$$f(C_o) = \frac{d}{dC_o}[C_og(C_o)]. \quad (17)$$

Hence, equation (16) may be transformed to a differential equation for g of the form

$$\frac{dg(C_o)}{dC_o} = \frac{g}{C_o}\left[\frac{\frac{5}{27}}{1 - \frac{3}{5}\frac{F(C_o)}{g}} - 1\right]. \quad (18)$$

On putting

$$g(C_o) = \exp[q(C_o)], \quad (19)$$

this equation changes to the equation for q of the form

$$\frac{dq(C_o)}{dC_o} = \frac{1}{C_o}\left[\frac{\frac{5}{27}}{1 - \frac{3}{5}F(C_o)e^{-q}} - 1\right]. \quad (20)$$

It is also shown from equation (6) that

$$\lim_{C_o\to 0} g(C_o) = 1, \quad (21)$$

so that

$$\lim_{C_o\to 0} q(C_o) = 0. \quad (22)$$

This gives the initial condition for integrating equation (20) with respect to q.

Since, in general, dq/dC_o must remain finite for any C_o, the following relation must hold:

$$\lim_{C_o \to 0} \left[\frac{\frac{5}{27}}{1 - \frac{3}{5} F(C_o) e^{-q(C_o)}} - 1 \right] = 0,$$

whence, on considering condition (22), we obtain

$$\lim_{C_o \to 0} F(C_o) = \frac{110}{81}.$$

Combining this with equation (14), there results an equation for determining the value of $D(0)$—namely,

$$D(0) = \frac{81}{110} \lim_{C_o \to 0} \left[\frac{K(C_o)}{C_o} \right]^2. \tag{23}$$

The corresponding equation for $D(0)$ derived in the previous paper, without making such an approximation as given above, is written

$$D(0) = \frac{1}{1.334} \lim_{C_o \to 0} \left[\frac{K(C_o)}{C_o} \right]^2. \tag{24}$$

Comparison of equations (23) and (24) shows that the present $D(0)$ equation differs in its numerical factor from the previous one only by about 1.8%. Such a slight difference may be neglected for most practical purposes. It is also shown that this numerical difference gives a measure of the degree of approximation of equation (20) for the case $y \to 1$—that is, the case of a constant diffusion coefficient. As understood from the process of deriving equation (20), the error involved in the equation becomes less as values of y become smaller in comparison with unity. Consequently, the method presented in this paper may be expected to give better results as the concentration increase of $D(C)$ becomes greater. However, it must be noted that at the same time the reliability of the method of moments underlying the present method becomes more doubtful.

Combining equations (17) and (20), we obtain

$$f(C_o) = \frac{\frac{5}{27} e^{q(C_o)}}{1 - \frac{3}{5} F(C_o) e^{-q(C_o)}},$$

so that

$$D(C_o) = \frac{\frac{5}{27} D(0) e^{q(C_o)}}{1 - \frac{3}{5} F(C_o) e^{-q(C_o)}}. \tag{25}$$

If equation (20) be integrated to give $q(C_o)$ with the initial condition (22) after determining the $F(C_o)$ plot from the experimentally given $K(C_o)$ curve, with $D(0)$ obtained by equation (23), we can immediately obtain the $D(C)$ plot without employing any ambiguous operations such as a graphical differentiation.

It may be convenient to summarize the whole process of our method. It is as follows: (*1*) plot $[K(C_o)/C_o]^2$ against C_o from the sorption data; (*2*) find by extrapolation the value of $[K(C_o)/C_o]^2$ at $C_o = 0$; (*3*) evaluate $D(0)$ from equation (23); (*4*) substitute $D(0)$ thus obtained into equation (14), and plot F against C_o; (*5*) integrate equation (20) with the initial condition (22) to obtain $q(C_o)$; (*6*) substitute $q(C_o)$ thus obtained, along with $D(0)$ and $F(C_o)$, into equation (25). Then the required D-C relation is obtained.

In integrating equation (20), graphical methods are usually most convenient for practical purposes, because F-C_o plots generally cannot be determined from experimental data with accuracy high enough to justify the use of numerical methods of integration.

Two limitations must be considered in applying this method practically. The first is that this method may essentially be applied only to systems in which diffusion coefficients satisfy the condition that $y < 1$. For many polymer-solvent systems, the diffusion coefficients are known generally to increase monotonously with increasing concentration. Therefore, this condition may not be so great a restriction for practical interest. The second limitation is the reliability of the method of moments underlying the present method for cases of diffusion coefficients varying over a great range. According to a separate investigation [4] concerning some unidimensional concentration-dependent diffusions in a semi-infinite medium, the method of moments can give approximate solutions which are useful enough for practical purposes, even for $D(C)$ increasing by factors of about 30 or so, but beyond these limits it ceases to be effective for quantitative treatments. It must be said, therefore, that the present method for determining concentration-dependent diffusion coefficients has a considerable limitation with respect to the applicable range of variation of $D(C)$. Although the ingenious method of Crank and Park [2] is free from such limitations as involved in our method, it requires a laborious iterative integration of a certain

nonlinear differential equation, and is therefore not convenient for rapid evaluation of the form of $D(C)$. Regarding this point, our method is far more advantageous, and is suitable for practical purposes if the degree of accuracy desired is not so high.

Applications

There are few reports on sorption experiments from which relevant $K(C_o)$ data are available. Only the following two sets of data have been available to the present authors: Prager's data for the system polyisobutylene-isobutane [7], and Crank and Park's data for the system polystyrene-chloroform [2]. These data have already been analyzed in detail by the respective authors using their own methods for determining the D-C relation. The problem to be considered next is the application of our method to these experimental data in the hope of checking its validity by comparing the results thus obtained with the corresponding existing ones.

The application of the method was first made to Prager's data. The results obtained are shown in Figure 1 with solid circles. In this figure, the values obtained by Prager with his own method using a step-function approximation and those by us in the previous paper are also plotted with open circles and crosses, respectively. It is seen that the results by these three different methods are in reasonably good accordance. This supports the validity of our present method.

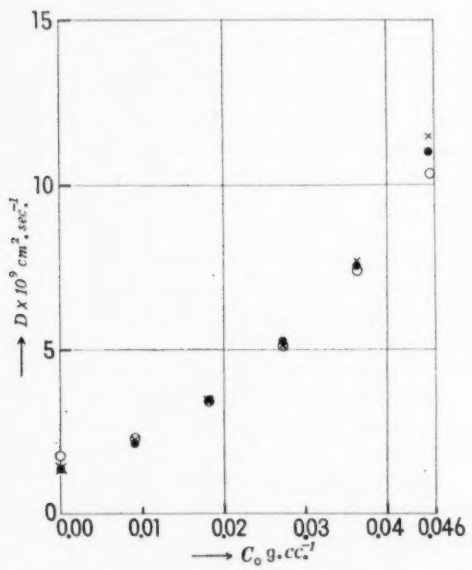

FIG. 1. *Application of the present method to Prager's data for the system polyisobutylene-isobutane: ●, present method; ○, Prager's method [7]; ×, authors' previous method [5].*

Crank and Park [2] have not given explicitly the $K(C_o)$ plot in their paper on the evaluation of the diffusion coefficient for the system polystyrene-chloroform. Instead, they have presented the values of $(t/l^2)_{\frac{1}{2}}$ as a function of C_o, where $(t/l^2)_{\frac{1}{2}}$ represents the time divided by the thickness of the sample sheet at which the sheet reached half the equilibrium sorption. From those data the required $K(C_o)$ plot can be obtained as follows. Equation (1) can be rewritten

$$Q_t = 2lC_o \frac{K(C_o)}{C_o} \sqrt{\frac{t}{l^2}}.$$

Since Q_∞, the equilibrium sorption attained theoretically after infinite time, can be represented by $2C_o l$, the above equation may be put in the form

$$\frac{Q_t}{Q_\infty} = \frac{K(C_o)}{C_o} \sqrt{\frac{t}{l^2}},$$

whence there follows the equation

$$K(C_o) = \frac{\frac{1}{2}C_o}{\sqrt{(t/l^2)_{\frac{1}{2}}}}. \tag{26}$$

This relation enables us to plot $K(C_o)$ against C_o when $(t/l^2)_{\frac{1}{2}}$ is known as a function of C_o. In deriving equation (26), it was assumed that equa-

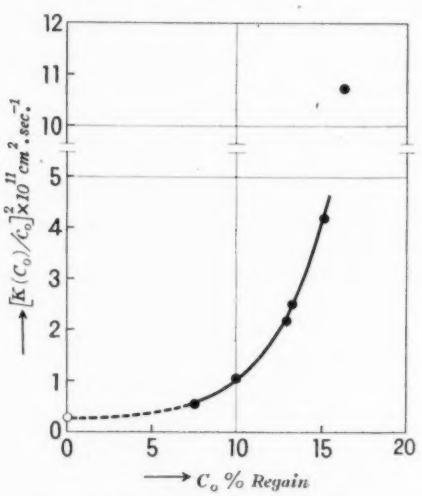

FIG. 2. $[K(C_0)/C_0]^2$ *plot for the system polystyrene-chloroform.*

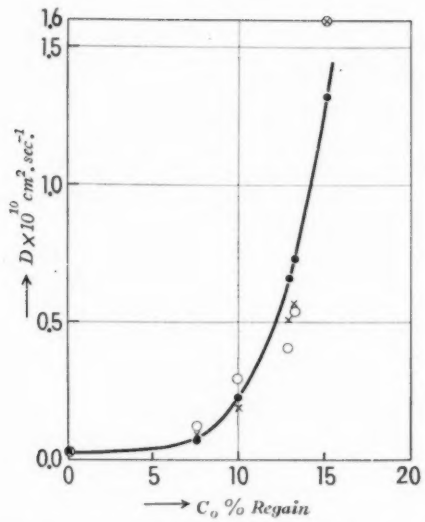

FIG. 3. *Application of the present method to Crank and Park's data for the system polystyrene-chloroform: ●, present method; ○, Crank and Park's method [2]; ×, Park's method [6].*

tion (1) may be applied up to the time of the half-sorption. This rather drastic assumption, however, appears to be justified according to a recent theoretical calculation by Crank [1] concerning the unidimensional diffusion equation with a discontinuously varying diffusion coefficient. Based on the $K(C_o)$ plot thus obtained, the $[K(C_o)/C_o]^2$ plot was constructed as shown in Figure 2. Since the lowest concentration at which Crank and Park's measurements were made was 7.5%, it was necessary to make a suitable extrapolation in order to determine the part of the plot for concentrations lower than this limit. An extrapolated curve is shown in Figure 2 with dotted line. Figure 3 shows the resultant *D-C* plot, together with those obtained by Crank and Park [2] (open circels) and by Park [6] (crosses); Park's values were evaluated by reanalyzing Crank and Park's original data using a more refined and reliable method. Although it may not be claimed that the agreement of our values with the others is satisfactory, the results obtained seem to be interesting and significant from the practical point of view. Considering the facility for application of our method, and allowing for the approximate nature of the method of moments, it may be regarded as rather striking that the present approximate method can be applied with this degree of accuracy to such a rapidly increasing diffusion coefficient.

Acknowledgment

The authors are largely indebted to Dr. J. Crank, Research Laboratory, Courtaulds Limited, England, for his interest and for encouragement shown to the work on the application of the method of moments to nonlinear diffusion problems.

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(Manuscript received November 17, 1952.)

Letters to the Editor

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Moisture Gradients in Centrifuged Samples

UNIVERSITY OF MANCHESTER
College of Technology
Manchester, England
July 22, 1952

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Welo, Ziifle, and McDonald in their article "Swelling Capacities of Fibers in Water: Part II: Centrifuge Studies" [9] described an interesting new freezing technique for measuring moisture gradients. They also discussed some of the data given in a recent paper of ours [7]. On the basis of this discussion they arrived at some deductions which call for comment. The theoretical treatment of Welo *et al.* has points of similarity with ours. It differs principally in considering the capillary water among fibers to be present as "aggregates," the volume of which is proportional to the cube of the linear dimensions of the air-water-fiber line at which surface tension acts. This consideration, among others, leads to two deductions which differ from ours. It introduces a two-thirds exponential into the effects of the centrifugal acceleration and, more important, it eliminates any consideration of a length factor independent of the dimensions of the air-water-fiber line which supports the capillary water. In our treatment we considered this independent length factor, which was effectively the dimension of the sample of fibers in the direction of the centrifugal acceleration. Our treatment starts from the assumption that in assemblies of hydrophilic fibers there are continuous water columns throughout. The basis for this assumption is well established. The earliest reference to it was made by Socrates in Plato's *Symposium* [3]. It is a traditional method of siphoning and filtering liquids from vessel to vessel [2]. An ordinary cotton cloth left hanging over the side of a bucket of water demonstrates the presence of continuous columns of water in the cloth; whether the cloth is crumpled or straight, after a short time the contents of the bucket are on the floor. In a rerent paper [6] it was shown that suction forces are capable of maintaining continuous columns of water even when opposed by forces equivalent to very large centrifugal fields. There is an elementary physics experiment which shows that capillary rise is independent of the straightness or crookedness of the capillary in the direction of the gravitational field, as shown in Figure 1. It is thus irrelevant whether the fibers, which have capillary channels between them, are convoluted or straight. The only important dimensions are: (*1*) the effective length of the air-water interface in a capillary, at *A* in Figure 1; and (*2*) the total height of the water column in a capillary, represented by *h* in Figure 1. Further experimental evidence in support of the concept of continuous columns of water throughout assemblies

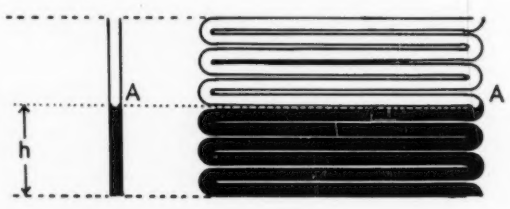

FIG. 1

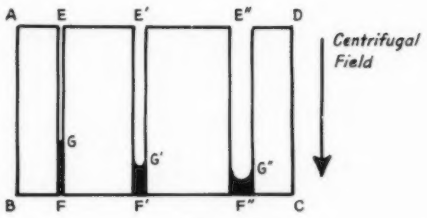

FIG. 2

of fibers is found in the solute migration phenomenon which occurs during the drying of moist textiles [4, 5].

It is clear that the greater the total height of the porous assembly of fibers in the direction of the centrifugal field, the smaller the fraction of the height filled by water with any particular magnitude of field and capillaries. Thus, the weight fraction of capillary water relative to the weight of fibers varies inversely as the height of the assembly of fibers in the direction of the field. This relationship is expressed in our paper [7]. Expressed differentially, it means that the water content increases from top to bottom of an assembly of fibers in the direction of the field, which can be either gravitational or centrifugal. The observation that the moisture content increases progressively in this direction, rather than suddenly, is explained as being due to the heterogeneous dimensions of the capillaries in an assembly of fibers [10]. This phenomenon is shown diagrammatically in Figure 2. Consider a moist hydrophilic porous mass, *ABCD*, in which three capillaries *EF*, *E'F'*, and *E"F"* of different lateral dimensions have been singled out for consideration. Imagine this porous mass placed in a centrifugal field; then the heights of each of the liquid columns *GF*, *G'F'*, and *G"F"* will be inversely proportional to the acceleration and to the transverse dimension of the capillary.

Two deductions can be made from this model immediately. One is that the moisture content increases in the direction of the centrifugal field, as given by Welo *et al.* in their Figure 7, but which they say cannot be explained satisfactorily. The same effect is also shown (see their Figures 1 and 2) in the much lower water retention of those oriented samples which have a much larger dimension in the direction of the centrifugal field since a smaller proportion of each capillary is filled in the samples with a larger dimension in the direction of the field. The other deduction is that the amount of water (which is proportional to the height of the water column) is inversely proportional to the acceleration, a fact shown in all of their S^2 *versus* R curves. At infinite acceleration the capillary water would be zero in the idealized case. Thus, in order to determine the amount of water in the fibers, which causes swelling, the extrapolation should be made in the direction of infinite acceleration, and not towards zero acceleration as given in their paper. This can be done if the S^2 data are plotted as reciprocals.

In analyzing our data in their Table III, Welo *et al.* [9], using their theoretical model and some regain data from their desiccation rate technique measurements [8], arrived at values for the capillary water. In a recent paper [1], Ashpole suggested that the saturation regains are very much nearer to the centrifuge values than their desiccation rate data suggest. It seems likely that the capillary water lies somewhere between the very low values indicated by Ashpole [1] and the very high values indicated by Welo *et al.* [9], and probably nearer to the values indicated in our paper [7].

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Group 3 will embrace discussions on the chemistry of lignin, its behavior in the pulping processes, and its utilization.

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